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ON WARING'S PROBLEM FOR CUBES.

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§1. *Introduction.*

THE object of this paper is to prove that almost all numbers are expressible as a sum of four non-negative cubes (of integers) provided the following hypothesis is true :

$$\text{(H)} \qquad \sum_{N=1}^{x} r_3^2(N) = O\left(x^{\frac{7}{6}-\epsilon}\right)$$

for any positive ϵ. Here $r_3(N)$ denotes the number of ways in which N is a sum of 3 non-negative cubes. The same result was proved by Hardy and Littlewood on the assumption of the hypothesis

$$r_3(N) = O(N^{\epsilon})$$

for any $\epsilon > 0$. Mahler has recently proved that this hypothesis is false. In fact Mahler[1] proved that

$$r_3(N) = \Omega\left(N^{\frac{1}{12}}\right)$$

[$f(x) = \Omega\{g(x)\}$ means that there exists an absolute positive constant c such that $\left|\frac{f(x)}{g(x)}\right| > c$ for infinitely many integer values of x.]

Let us denote the following hypotheses by the capital letters used before them :

(A) : *Almost all numbers are sums of four cubes of integers* $\geqslant 0$.

$$\text{(B)} : \qquad r_3(N) = O\left(N^{\frac{1}{6}-\epsilon}\right)$$

for any positive ϵ.

$$\text{(H)} : \qquad \sum_{N=1}^{x} r_3^2(N) = O\left(x^{\frac{7}{6}-\epsilon}\right)$$

for any positive ϵ.

Then our result takes the form

THEOREM I. (H) $\longrightarrow$ (A).

[1] *Jour. London Math. Soc.*, 1936, **11**, 136–138.

Since, assuming (B) *we obtain*

$$\sum_{N=1}^{x} r_3^2(N) \leq \max_{1 \leqslant N \leqslant x} r_3(N) \sum_{1}^{x} r_3(N)$$

$$= O(x^{\frac{1}{6}-\epsilon}) \times O(x) = O(x^{\frac{7}{6}-\epsilon})$$

it follows that

$$(B) \longrightarrow (H)$$

[(A) → (B) is used to denote that the relation (A) implies (B). The symbol is not commutative, for it does not follow that (B) → (A).]

From this relation and Theorem I it follows that

THEOREM II. (B) —→ (A).

We can also express this result by saying that at least one of the hypotheses (A) and (B) is true, or thus :

THEOREM III. *At least one of the following results* [(a) *and* (b)] *is true* :

(*a*) *Almost all numbers are sums of four cubes of integers* $\geqslant 0$

(*b*) $r_3(N) = \Omega(N^{\frac{1}{6}-\epsilon})$

for every positive ϵ.

In conclusion we observe that although (H) is an unproved result, it is trivial that

$$\sum_{1}^{x} r_3^2(N) \leq \max_{1 \leqslant N \leqslant x} r_3(N) . \sum_{N \leqslant x} r_3(N)$$

$$= O(x^{\frac{1}{3}+\epsilon}) \times O(x) = O(x^{\frac{8}{6}+\epsilon})$$

for any $\epsilon > 0$.

We use Gelbeke's method to prove our results.

§2. *Notation.*

$r_s(n)$ is equal to the number of solutions of

$$n = h_1^3 + h_2^3 + \ldots + h_s^3, \quad h_i \geqslant 0 \qquad (i = 1, 2, \ldots, s)$$

$$k = 3, \; K = 2^{k-1} = 4.$$

$$\rho = e^{2\pi i \frac{l}{q}}, \qquad (l, q) = 1,$$

$$S_\rho = \sum_{z=1}^{q} \rho^{z^3}$$

$$A(q, j) = q^{-4} \sum_{\rho} (S_\rho)^4 \rho^{-j}$$

$$S(j, \lambda) = \sum_{q=1}^{\lambda} A(q, j)$$

$$f(x) = \sum_{h=0}^{n^{\frac{1}{3}}} x^{h^3}$$

$$a = \frac{1}{k} = \tfrac{1}{3}$$

$$\psi_\rho(x) = \Gamma(1+a)\frac{S_\rho}{q}\left\{1 + \sum_{j=1}^{n} \frac{a(a+1)\cdots(a+j-1)}{j!}\left(\frac{x}{\rho}\right)^j\right\}$$

$$\phi_\rho(x) = \Gamma(1+a)\frac{S_\rho}{q}\sum_{j=n+1}^{\infty} \frac{a(a+1)\cdots(a+j-1)}{j!}\left(\frac{x}{\rho}\right)^j$$

$$W_\rho(x) = \psi_\rho(x) + \phi_\rho(x) = \Gamma(1+a)\frac{S_\rho}{q}\left(1 - \frac{x}{\rho}\right)^{-a}$$

We write hypothesis (H) in the following form

$$\sum_{n=1}^{x} r_3^2(n) = O(x^{\frac{7}{6}-\epsilon_2})$$

where ϵ_2 is a fixed (but arbitrary) positive number.

$$\left.\begin{aligned}\theta &= \cdot 8\\ \delta &= \tfrac{3}{8}\end{aligned}\right\}$$

ϵ's are arbitrary positive numbers.

C's are arbitrary positive numbers depending at most on ϵ. ϵ_1 and ϵ_2 are fixed (but arbitrary) positive numbers such that $\epsilon_2 > 3\epsilon_1$.

§3. *Farey-Dissection.*

On the circle $|x| = 1$ we mark off the points $\rho = e^{2\pi i \frac{l}{q}}$, which correspond to the Farey fractions with denominators $\leq n^{1-a}$, and we divide the circle into arcs by the mediants between neighbouring fractions. It is known that the arc which contains the point ρ, stretches on either side of this point by something not more than $\frac{2\pi}{qn^{1-a}}$ and not less than $\frac{\pi}{qn^{1-a}}$. The arcs which correspond to $n^{\frac{1}{3}-\epsilon_1} \leqslant q \leqslant n^{\frac{3}{8}}$ are called m-arcs (minor arcs) and those which correspond to $1 \leq q < n^{\frac{1}{3}-\epsilon_1}$ are called M-arcs (major arcs). The M-arcs are subdivided in the following manner. The part of the M-arc which does not stretch for more than $\frac{\pi}{q^\theta n^{1-\theta a}}$ on each side of ρ will be denoted by M_1, the rest of the M-arc (always existent) is called an M_2-arc.

$$\left[\text{for } \frac{\pi}{q^\theta n^{1-\theta a}} < \frac{\pi}{qn^{1-a}} \quad \text{so long as } q < n^a\right]$$

§4. *Well-Known Lemmas*

THEOREM 1.[2] *Let* $|y| \leqslant \frac{1}{2}$ *and* $a_0 \geqslant a_1 \geqslant \ldots \geqslant 0$. *Then*

$$\left| \sum_{j=0}^{N} a_j e^{2\pi i y j} \right| \leqslant \frac{a_0}{\sin \pi |y|}$$

THEOREM 2.[3]

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} \left| \sum_{j=0}^{N} a_j e^{2\pi i y j} \right|^2 dy = \sum_{j=0}^{N} |a_j|^2$$

THEOREM 3.[4] *For* $\beta > 0$ *and integral* $j > 0$,

$$\left| \frac{\Gamma(1+\beta+j)}{j!} - j^{\beta} \right| < \gamma(\beta)\, j^{\beta-1}$$

where $\gamma(\beta)$ *depends only on* β, *not on* j.

THEOREM 4.[5] *For* $m > 0$, r *an integer*,

$$\left| \sum_{k=r+1}^{r+m} \rho^{k^k} \right|^K < Cq^{\epsilon} m^{\epsilon} \left(m^{K-1} + \frac{m^K}{q} + q m^{K-k} \right)$$

THEOREM 5.[6] $|S_\rho| < Cq^{1-a}$.

§5.

THEOREM 6. *On the whole circle* $|x| = 1$ *we have*

$$|\psi_\rho(x)| < Cn^{\frac{1}{3}} q^{-\frac{1}{3}}$$

Proof:

$$\psi_\rho(x) = \frac{S_\rho}{q} \left\{ \Gamma(1+a) + a \sum_{j=1}^{n} \frac{\Gamma(1+a+j)}{j!\,(a+j)} \left(\frac{x}{\rho}\right)^j \right\}$$

Applying Theorems 3 and 5 we get

$$|\psi_\rho(x)| < Cq^{-\frac{1}{3}} \left\{ \Gamma(1+a) + a \sum_{j=1}^{n} (j^{a-1} + \gamma(a)\, j^{a-2}) \right\}$$

$$< Cn^{\frac{1}{3}} q^{-\frac{1}{3}}$$

THEOREM 7. *Let*

$$\frac{x}{\rho} = e^{2\pi i y}, \quad |y| \leqslant \tfrac{1}{2}.$$

---

[2] E. Landau, *Vorlesungen über Zahlentheorie* 1, satz 140 with $R(w) = \sum_{j=0}^{j=w} e^{2\pi i y j}$.

[3] *Ibid.*, satz 223.

[4] *Ibid.*, satz 277.

[5] *Ibid.*, satz 267.

[6] *Ibid.*, Band 1, satz 315.

Then

$$\phi_\rho(x) < Cn^{-\frac{2}{3}}\, q^{-\frac{1}{3}}\, |y|^{-1}$$

$$|W_\rho(x)| < Cq^{-\frac{1}{3}}\, |y|^{-\frac{1}{3}}$$

Proof: Applying Theorems 1, 3 and 5 we have

$$|\phi_\rho(x)| < Cq^{-\frac{1}{3}}\, \Gamma(1+a) \left| \sum_{j=n+1}^{\infty} \frac{a(a+1)\cdots(a+j-1)}{j!} \left(\frac{x}{\rho}\right)^j \right|$$

$$< Cq^{-\frac{1}{3}}\, \Gamma(1+a)\, \frac{a(a+1)\cdots(a+n)}{(n+1)!}\, \frac{1}{\sin \pi |y|}$$

$$= Cq^{-\frac{1}{3}}\, \frac{a}{n+1}\, \frac{\Gamma(1+a+n)}{n!}\, \frac{1}{\sin \pi |y|}$$

$$< Cq^{-\frac{1}{3}}\, |y|^{-1}\, n^{-\frac{2}{3}}$$

From Theorem 5 it follows that

$$|W_\rho(x)| = \left| \Gamma(\tfrac{4}{3})\, \frac{S_\rho}{q} \left(1 - \frac{x}{\rho}\right)^{-a} \right| < Cq^{-\frac{1}{3}}\, |y|^{-\frac{1}{3}}$$

THEOREM 8. *Let*

$$\frac{x}{\rho} = e^{2\pi i y},\ |y| \leqslant \tfrac{1}{2},$$

Then

$$|\psi_\rho(x)| < Cq^{-\frac{1}{3}}\ \mathrm{Min}\ (n^{\frac{1}{3}},\ |y|^{-\frac{1}{3}})$$

Proof:

For $|y| \leqslant \frac{1}{n}$ the result follows from Theorem 6.

For $|y| > \frac{1}{n}$ the result follows from Theorem 7

for

$$|\psi_\rho(x)| \leqslant |W_\rho(x)| + |\phi_\rho(x)|$$

$$< Cq^{-\frac{1}{3}}\, y^{-\frac{1}{3}} + Cn^{-\frac{2}{3}}\, q^{-\frac{1}{3}}\, |y|^{-1} < Cq^{-\frac{1}{3}}\, |y|^{-\frac{1}{3}}$$

THEOREM 9.

$$\int_{C-M_1} |\psi_\rho^4(x)|^2\, |dx| < Cn^{\frac{5}{3}-\frac{5}{3}\theta a}\, q^{-\frac{8}{3}+\frac{5}{3}\theta}$$

In the integral C *denotes the circle* $|x| = 1$.

Proof:

$$q < n^{\frac{1}{3}-\epsilon_1},\ \frac{1}{2n} < \frac{1}{2q^\theta\, n^{1-\theta a}} < \frac{1}{2qn^{1-a}}$$

for

$$q^\theta < n^{\theta a} \text{ and } q^{1-\theta} < n^{a(1-\theta)}$$

as long as $q < n^a$

$$\int_{C-M_1} |\psi_\rho^4(x)|^2\, |dx| < Cq^{-\frac{8}{3}} \int_{\frac{1}{2q^\theta\, n^{1-\theta a}}}^{\infty} y^{-\frac{8}{3}}\, dy < Cq^{-\frac{8}{3}+\frac{5}{3}\theta}\ n^{\frac{5}{3}-\frac{5}{3}\theta a}$$

§6. *Lemmas for the* m-*Arcs.*

THEOREM 10. *On* m,

$$|f(x)| < Cn^{\frac{1}{4}+\frac{5}{4}\epsilon_1+\epsilon}$$

Proof:

$$\text{Put } t(j) = \sum_{k=0}^{j^3} \rho^{k^3} \text{ for } j \geqslant 0, \quad t(-1) = 0$$

Then

$$f(x) = \sum_{k=0}^{n^{\frac{1}{3}}} \rho^{k^3}\left(\frac{x}{\rho}\right)^{k^3} = \sum_{j=0}^{n} c_j \rho^j \left(\frac{x}{\rho}\right)^j$$

(where $c_j = 1$ if $j = y^3$ and otherwise $c_j = 0$)

$$= \sum_{j=0}^{n} \left\{t(j) - t(j-1)\right\}\left(\frac{x}{\rho}\right)^j$$

$$= \sum_{j=0}^{n-1} t(j) \left\{\left(\frac{x}{\rho}\right)^j - \left(\frac{x}{\rho}\right)^{j+1}\right\} + t(n) \left(\frac{x}{\rho}\right)^n$$

$$= \left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} \left(\frac{x}{\rho}\right)^j t(j) + t(n) \left(\frac{x}{\rho}\right)^n$$

Now

$$\left|\arg \frac{x}{\rho}\right| < \frac{2\pi}{qn^{1-a}}$$

whence

$$\left|1 - \frac{x}{\rho}\right| < \frac{2\pi}{qn^{1-a}}$$

(as length of the chord). By Theorem 4,

$$|t(j)|^4 < Cn^{\epsilon}\{n + n^{1+\epsilon_1} + n\} < Cn^{1+\epsilon_1+\epsilon}$$

and therefore

$$|t(j)| < Cn^{\frac{1}{4}+\frac{\epsilon_1}{4}+\epsilon}$$

Hence

$$|f(x)| < \left(\frac{2\pi n}{qn^{1-a}} + 1\right) Cn^{\frac{1}{4}+\frac{\epsilon_1}{4}+\epsilon} < Cn^{\frac{1}{4}+\frac{5\epsilon_1}{4}+\epsilon}$$

THEOREM 11. *If Hypothesis* (*H*) *is true then*

$$\sum_m \int_m |f^4(x)|^2 \, |dx| < Cn^{\frac{5}{3}+3\epsilon_1-\epsilon_2+\epsilon}$$

Proof:

$$\sum_m \int_m |f^4(x)|^2 \, |dx| < \text{Max } |f(x)|^2 \int_{-\frac{1}{2}}^{\frac{1}{2}} |f^3(e^{2\pi i y})|^2 \, dy$$

where Max $|f(x)|$ denotes the maximum value of $|f(x)|$ on m.

$$f^3(x) = \sum_{j=0}^{3n} \mathrm{R}(j)\, x^j$$

where $0 \leqslant \mathrm{R}(j) \leqslant r_3(j)$
so that using Theorem 2 we have

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} |f^3(e^{2\pi i y})|^2\, dy \leqslant \sum_{j=0}^{3n} |r_3(j)|^2 < \mathrm{C}n^{\frac{7}{6}-\epsilon_2},$$

using our Hypothesis (H) as mentioned in §2;
and finally, using Theorem 10,

$$\sum_m \int_m |f^4(x)|^2\, |dx| < \mathrm{C}n^{\frac{1}{2}+3\epsilon_1+\epsilon} \cdot n^{\frac{7}{6}-\epsilon_2} < \mathrm{C}n^{\frac{5}{3}+(3\epsilon_1-\epsilon_2)+\epsilon}$$

§7. *Lemmas for the M_1-Arcs.*

THEOREM 12. *If*

$$\frac{x}{\rho} = e^{2\pi i y},\ |y| \leqslant \tfrac{1}{2}$$

Then

$$|f(x) - \psi_\rho(x)| < \mathrm{C}q^{\frac{3}{4}+\epsilon} \operatorname{Max}(n|y|, 1)$$

Proof:

$$f(x) = \left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} t(j) \left(\frac{x}{\rho}\right)^j + t(n) \left(\frac{x}{\rho}\right)^n$$

$$\psi_\rho(x) = \Gamma(1+a)\, \frac{\mathrm{S}_\rho}{q} \left[1 + \sum_{j=1}^{n} \frac{a(a+1)\cdots(a+j-1)}{j!} \left(\frac{x}{\rho}\right)^j\right]$$

$$= \Gamma(1+a)\, \frac{\mathrm{S}_\rho}{q} \left\{u(0) + [u(1) - u(0)] \left(\frac{x}{\rho}\right) + \cdots + [u(n) - u(n-1)] \left(\frac{x}{\rho}\right)^n\right\}$$

$$\left(\text{where } u(j) = \frac{(a+1)(a+2)\cdots(a+j)}{j!} \text{ for } j > 0 \text{ and } u(0) = 1\right)$$

$$= \Gamma(1+a)\, \frac{\mathrm{S}_\rho}{q} \left\{\left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} u(j) \left(\frac{x}{\rho}\right)^j + u(n) \left(\frac{x}{\rho}\right)^n\right\}$$

$$= \frac{\mathrm{S}_\rho}{q} \left\{\left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} \frac{\Gamma(1+a+j)}{j!} \left(\frac{x}{\rho}\right)^j + \frac{\Gamma(1+a+n)}{n!} \left(\frac{x}{\rho}\right)^n\right\}$$

$$= \left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} v(j) \left(\frac{x}{\rho}\right)^j + v(n) \left(\frac{x}{\rho}\right)^n$$

$$\text{where} \qquad v(j) = \frac{\mathrm{S}_\rho}{q} \frac{\Gamma(1+a+j)}{j!} \qquad (0 \leqslant j \leqslant n)$$

$t(j)$ can be divided into $\left[\frac{j^a}{q}\right]$ parts each equal to S_ρ, *plus* at most

$[j^a] + 1 - \left[\frac{j^a}{q}\right] q \leqslant q$ further terms. Hence by Theorem 4,

$$\left| t(j) - \left[\frac{j^a}{q}\right] S_\rho \right| < Cq^{\frac{3}{4}+\epsilon}$$

since

$$\left| \sum_{h=1}^{m} \rho^{h^2} \right| \leqslant \sum_{h=1}^{m} 1 \leqslant q^{\frac{1}{2}} \text{ if } m \leqslant q^{\frac{1}{2}}$$

and

$$\left| \sum_{h=1}^{m} \rho^{h^2} \right|^4 < Cq^{\epsilon}(m^2) < Cq^{3+\epsilon} \text{ if } q^{\frac{1}{2}} < m \leqslant q$$

whence

$$\left| t(j) - \frac{j^a}{q} S_\rho \right| < Cq^{\frac{3}{4}+\epsilon} + |S_\rho| < Cq^{\frac{3}{4}+\epsilon}$$

Further by Theorem 3,

$$\left| \frac{\Gamma(1+a+j)}{j!} - j^a \right| < C$$

so that

$$\left| v(j) - j^a \frac{S_\rho}{q} \right| < C$$

Thus we obtain

$$|t(j) - v(j)| = \left| \left(t(j) - j^a \frac{S_\rho}{q} \right) - \left(v(j) - j^a \frac{S_\rho}{q} \right) \right|$$

$$< Cq^{\frac{3}{4}+\epsilon}$$

and hence

$$|f(x) - \psi_\rho(x)| = \left| \left(1 - \frac{x}{\rho}\right) \sum_{j=0}^{n-1} \left(t(j) - v(j) \right) \left(\frac{x}{\rho}\right)^j + \left(t(n) - v(n) \right) \left(\frac{x}{\rho}\right)^n \right|$$

$$< C(n|y| + 1)\, q^{\frac{3}{4}+\epsilon} < Cq^{\frac{3}{4}+\epsilon} \operatorname{Max}(n|y|, 1)$$

THEOREM 13.

$$\sum_{M_1} \int_{M_1} |f^4(x) - \psi_\rho{}^4(x)|^2 |dx| < Cn^{\frac{5}{3}+\epsilon-\theta\epsilon_1}$$

Proof:

Put $f(x) - \psi_\rho(x) = V_\rho(x)$

Then

$$|f^4(x) - \psi_\rho{}^4(x)|^2 = |[V_\rho(x) + \psi_\rho(x)]^4 - \psi_\rho{}^4(x)|^2$$

$$= |V_\rho(x)|^2 |V_\rho{}^3(x) + 4V_\rho{}^2(x)\psi_\rho(x) + 6V_\rho(x)\psi_\rho{}^2(x) + 4\psi_\rho{}^3(x)|^2$$

$$< C|V_\rho(x)|^8 + C|V_\rho(x)|^2 |\psi_\rho(x)|^6$$

where

$$|V_\rho(x)| < Cq^{\frac{3}{4}+\epsilon} \operatorname{Max}(n|y|, 1) \text{ by Theorem 12.}$$

Hence

$$\int_{M_1} |f^4(x) - \psi\rho^4(x)| \, |dx|$$

$$< C \int_{M_1} |V\rho(x)|^8 \, |dx| + C \int_{M_1} |V\rho(x)|^2 \, |\psi\rho(x)|^6 \, |dx|$$

$$< Cq^{6+\epsilon} \int_0^{\frac{1}{n}} dy + Cn^8 q^{6+\epsilon} \int_{\frac{1}{n}}^{\frac{1}{2q^\theta n^{1-\theta a}}} y^8 \, dy$$

$$+ Cq^{\frac{8}{3}-2+\epsilon} \cdot n^2 \int_0^{\frac{1}{n}} dy + Cq^{\frac{8}{3}-2+\epsilon} \cdot n^2 \int_{\frac{1}{n}}^{\frac{1}{q^\theta n^{1-\theta a}}} dy$$

$$< C \left\{ \frac{q^{6+\epsilon}}{n} + \frac{q^{6-9\theta+\epsilon}}{n^{1-9\theta a}} + nq^{-\frac{1}{3}+\epsilon} + q^{-\frac{1}{3}-\theta+\epsilon} \cdot n^{1+\theta a} \right\}$$

Hence,

$$\sum_{M_1} \int_{M_1} |f^4(x) - \psi\rho^4(x)|^2 \, |dx|$$

$$< C \left\{ \frac{n^{(\frac{1}{3}-\epsilon_1)(8+\epsilon)}}{n} + \frac{n^{(\frac{1}{3}-\epsilon_1)(8-9\theta+\epsilon)}}{n^{1-9\theta a}} + n \cdot n^{(\frac{1}{3}-\epsilon_1)(\frac{8}{3}+\epsilon)} \right.$$

$$\left. + n^{1+\theta a} \cdot n^{(\frac{8}{3}-\theta+\epsilon)(\frac{1}{3}-\epsilon_1)} \right\}$$

$$< C \left\{ n^{\frac{8}{9}-8\epsilon_1+\epsilon} + n^{\frac{8}{9}-\theta\epsilon_1+\epsilon} + n^{\frac{8}{9}-\frac{8}{3}\epsilon_1+\epsilon} + n^{\frac{8}{3}-\epsilon_1(\frac{8}{3}-\theta)+\epsilon} \right\}$$

$$< Cn^{\frac{8}{9}-\theta\epsilon_1+\epsilon}$$

§8. *Lemmas for the M_2-Arcs.*

THEOREM 14. *Let*

$$\frac{x}{\rho} = e^{2\pi i y}, \; |y| \leqslant \tfrac{1}{2}$$

Then on an M_2-arc,

$$|f(x)| < Cn^{\frac{1}{12}+\epsilon} \cdot q^{-\frac{1}{4}-\epsilon} \, |y|^{-\frac{1}{4}-\epsilon}$$

Proof:

$$x = e^{2\pi i \left(\frac{l}{q}+y\right)}, \; 1 \leqslant q < n^{\frac{1}{3}-\epsilon_1}$$

$$\frac{1}{2q^\theta n^{1-\theta a}} \leqslant |y| < \frac{1}{qn^{1-a}} \text{ and } \frac{2}{q|y|} > 1$$

since

$$\frac{2}{q|y|} > \frac{2}{q \cdot \frac{1}{qn^{1-a}}} = 2n^{1-a} > 2.$$

By the theory of Farey fractions there exist three numbers l_1, q_1, y_1 satisfying the following conditions :

$$\frac{l_1}{q_1} + y_1 = \frac{l}{q} + y$$

$$0 \leq l_1 \leq q_1 \leq \frac{2}{q|y|}, \qquad (l_1, q_1) = 1$$

$$|y_1| < \frac{q|y|}{2q_1} \leq \frac{1}{q_1^2}$$

since

$$2\pi |y_1| < \frac{2\pi}{q_1 \frac{2}{q|y|}} = \frac{2\pi q |y|}{2q_1}$$

and

$$\frac{q|y|}{2q_1} \leqslant \frac{2}{2q_1^2} = \frac{1}{q_1^2}$$

Here $n^{\frac{1}{3}-\epsilon_1} \leq q_1 \leq n^{\frac{2}{3}}$ is impossible, for then,

$$|y_1| < \frac{q|y|}{2q_1} < \frac{1}{2q_1 n^{\frac{2}{3}}}$$

so that x would belong to an m-arc. Let, now, $n > 8$. Then $1 \leqslant q_1 < n^{a-\epsilon_1}$ is impossible, for if not we would have

$$|lq_1 - l_1 q| = qq_1 |y_1 - y| \leqslant qq_1 |y| + qq_1 |y_1|$$

$$< qq_1 |y| + qq |y| \quad \left(\text{since } q_1 |y_1| < \frac{q|y|}{2}\right)$$

$$= q(q_1 + q)|y| < \frac{2n^{\frac{1}{3}-\epsilon_1} q}{q^{n^{\frac{2}{3}}}} \leqslant \frac{2n^{-\epsilon_1}}{n^{\frac{1}{3}}} < 1$$

But this implies

$$lq_1 - l_1 q = 0, \; q = q_1, \; l = l_1, \; y = y_1$$

and therefore

$$|y_1| = \frac{q|y|}{q_1} > \frac{q|y|}{2q_1}$$

contradicting our hypothesis.

Hence $q_1 > n^{\frac{2}{3}}$.

Putting $\rho_1 = e^{2\pi i \frac{l_1}{q_1}}$ we obtain by Theorem 4,

$$\max_{0 \leqslant j \leqslant n} |t_1(j)| = \left| \sum_{k=0}^{a}{}' \rho_1^{k^3} \right| < Cn^{\frac{1}{2}+\epsilon} \; q_1^{\frac{1}{4}+\epsilon}$$

since

$$\left|\sum_{h=0}^{n^a} \rho_1 h^3\right|^4 < Cq_1^{\epsilon} n^{\epsilon}\left(n + \frac{n^{\frac{4}{3}}}{q_1} + q_1 n^{\frac{1}{3}}\right)$$

$$< Cq_1^{\epsilon} n^{\epsilon} \cdot q_1 n^{\frac{1}{3}} \text{ since } q_1 > n^{\frac{2}{3}}$$

$$= Cq_1^{1+\epsilon} \cdot n^{\frac{1}{3}+\epsilon}$$

and hence

$$|t_1(j)| < Cn^{\frac{1}{12}+\epsilon}\left(\frac{2}{q|y|}\right)^{\frac{1}{4}+\epsilon} < Cn^{\frac{1}{12}+\epsilon} q^{-\frac{1}{4}-\epsilon} |y|^{-\frac{1}{4}-\epsilon}$$

But

$$f(x) = \left(1-\frac{x}{\rho_1}\right)\sum_{j=0}^{n-1} t_1(j)\left(\frac{x}{\rho_1}\right)^j + t_1(n)\left(\frac{x}{\rho_1}\right)^n$$

where

$$\left|1 - \frac{x}{\rho_1}\right| < 2\pi|y_1| < \frac{2\pi}{n^{\frac{4}{3}}}$$

$$|f(x)| \leqslant c\left(\frac{2\pi n}{n^{\frac{4}{3}}} + 1\right) n^{\frac{1}{12}+\epsilon} q^{-\frac{1}{4}-\epsilon} |y|^{-\frac{1}{4}-\epsilon}$$

$$< Cn^{\frac{1}{12}+\epsilon} q^{-\frac{1}{4}-\epsilon} |y|^{-\frac{1}{4}-\epsilon}.$$

Thus the theorem is proved for $n > 8$.

For $n \leq 8$ it is trivial.

THEOREM 15.

$$\sum_{M_2}\int_{M_2} |f^4(x)|^2 |dx| < Cn^{\frac{5}{3}-\epsilon_1\theta+16\epsilon}$$

Proof:

$$\int_{M_2} |f^4(x)|^2 |dx| < Cn^{\frac{8}{3}+8\epsilon} q^{-2-8\epsilon} \int_{\frac{1}{2q^\theta n^{1-\theta a}}}^{\infty} |y|^{-2-8\epsilon} dy$$

$$< Cn^{\frac{8}{3}+8\epsilon} q^{-2-8\epsilon} q^{\theta(1+8\epsilon)} n^{(1-\frac{\theta}{3})(1+8\epsilon)}$$

$$< Cn^{\frac{8}{3}-\frac{\theta}{3}+16\epsilon} q^{\theta-2}$$

$$\sum_{M_2}\int_{M_2} |f^4(x)|^2 |dx| < Cn^{\frac{5}{3}-\frac{\theta}{3}+16\epsilon} n^{\theta(\frac{1}{3}-\epsilon_1)}$$

$$< Cn^{\frac{5}{3}-\epsilon_1\theta+16\epsilon}$$

§9. *Lemmas for the Whole Circle.*

THEOREM 16.

$$\int_C |f^4(x) - \sum_{q \leqslant n^{\delta a}} \psi\rho^4(x)|^2 |dx| = 0\,(n^{\frac{5}{3}})$$

[In other words the left side divided by $n^{\frac{5}{3}}$ tends to zero.]

Proof:

$$\int_C |f^4(x) - \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx|$$

$$= \sum_{m\,m} \int |f^4(x) - \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx| + \sum_{M_2\,M_2} \int |f^4(x) - \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx|$$

$$+ \sum_{M_1\,M_1} \int |f^4(x) - \sum_{q \leqslant n^{\delta a}}{}' \psi_\rho^4(x) - \psi_\rho^4(x)|^2 \, |dx|$$

($\sum_{q=1}^{n^{\delta a}}{}'$ here denotes $\sum_{q=1}^{n^{\delta a}}$ *minus* that term of the sum $\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)$ which corresponds to the arc M_1).

We now apply the theorem

$$|\sum_{j=1}^{N} \xi_j|^2 \leq N \sum_{j=1}^{N} |\xi_j|^2$$

which follows from

$$|\xi_i| \, |\xi_j| \leq \frac{|\xi_i|^2 + |\xi_j|^2}{2}$$

and obtain (using $|a-b|^2 \leqslant 2|a|^2 + 2|b|^2$)

$$\int_C |f^4(x) - \sum_{q \leqslant n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx| \leq 2 \sum_{m\,m} \int |f^4(x)|^2 \, |dx|$$

$$+ 2 \sum_{m\,m} \int |\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx| + 2 \sum_{M_2\,M_2} \int |f^4(x)|^2 \, |dx|$$

$$+ 2 \sum_{M_2\,M_2} \int |\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx| + 2 \sum_{M_1\,M_1} \int |f^4(x) - \psi_\rho^4(x)|^2 \, |dx|$$

$$+ 2 \sum_{M_1\,M_1} \int |\sum_{q=1}^{n^{\delta a}}{}' \psi_\rho^4(x)|^2 \, |dx|.$$

From Theorems 11, 15, 13 the first, third and fifth expressions are together less than

$$Cn^{\frac{\delta}{3}} \, (n^{3\epsilon_1 - \epsilon_2 + \epsilon} + n^{-\epsilon_1 \theta + 10\epsilon})$$

The sum of the second, fourth and sixth expressions is equal to

$$2 \sum_{m\,m} \int |\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx| + 2 \sum_{M_2\,M_2} \int |\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx|$$

$$+ 2 \sum_{M_1'\,M_1'} \int |\sum_{q \leqslant n^{\delta a}}{}' \psi_\rho^4(x)|^2 \, |dx|$$

$$+ 2 \sum_{M_1''\,M_1''} \int |\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x) - \psi_\rho^4(x)|^2 \, |dx|$$

[Here $\mathfrak{M}_1'$ denotes those arcs $\mathfrak{M}_1$ which correspond to $q \leqslant n^{\delta a}$ and $\mathfrak{M}_1''$ denotes the remaining arcs. In the fourth expression the function $\psi_\rho^4(x)$ which corresponds to $\mathfrak{M}_1''$ is written separately. This term is not contained in $\sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x)$]

$$\leq 2 \sum_{m} \int_{m} \Big| \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x) \Big|^2 |dx| + 2 \sum_{\mathfrak{M}_2} \int_{\mathfrak{M}_2} \Big| \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x) \Big|^2 |dx|$$

$$+ 2 \sum_{\mathfrak{M}_1'} \int_{\mathfrak{M}_1'} \Big| \sum_{q=1}^{n^{\delta a}}{}' \psi_\rho^4(x) \Big|^2 |dx| + 4 \sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} \Big| \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(x) \Big|^2 |dx|$$

$$+ 4 \sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} |\psi_\rho^4(x)|^2 |dx|$$

$$\leq 4 n^{2\delta a} \left\{ \sum_{m} \int_{m} \sum_{q=1}^{n^{\delta a}} |\psi_\rho^4(x)|^2 |dx| \right.$$

$$\left. + \sum_{\mathfrak{M}_2} \int_{\mathfrak{M}_2} \sum_{q=1}^{n^{\delta a}} |\psi_\rho^4(x)|^2 |dx| + \sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} \sum_{q=1}^{n^{\delta a}} |\psi_\rho^4(x)|^2 |dx| \right\}$$

$$+ 4 n^{2\delta a} \sum_{\mathfrak{M}_1'} \int_{\mathfrak{M}_1'} \sum_{q=1}^{n^{\delta a}}{}' |\psi_\rho^4(x)|^2 |dx| + 4 \sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} |\psi_\rho^4(x)|^2 |dx|$$

$$= 4 n^{2\delta a} \sum_{\mathfrak{M}_1'} \int_{C - \mathfrak{M}_1'} |\psi_\rho^4(x)|^2 |dx| + 4 \sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} |\psi_\rho^4(x)|^2 |dx|.$$

From Theorem 9 follows

$$4 n^{2\delta a} \sum_{\mathfrak{M}_1'} \int_{C - \mathfrak{M}_1'} |\psi_\rho^4(x)|^2 |dx|$$

$$< C n^{\frac{5}{3} - \frac{5}{3}\theta a + 2\delta a} \sum_{q \leqslant n^{\delta a}} q^{-\frac{5}{3} + \frac{5}{3}\theta}$$

$$< C n^{\frac{5}{3} - \frac{5}{3}\theta a + 2\delta a} \cdot n^{\frac{2}{3}\cdot\delta a} < C n^{\frac{5}{3} - \frac{4}{9} + \frac{1}{3}} = C n^{\frac{5}{9} - \frac{1}{9}}$$

From Theorem 8 follows

$$\int_{\mathfrak{M}_1''} |\psi_\rho^4(x)|^2 |dx| < C q^{-\frac{2}{3}} n^{\frac{2}{3}} \int_0^{\frac{1}{n}} dy + C q^{-\frac{2}{3}} \int_{\frac{1}{n}}^{\infty} y^{-\frac{2}{3}} dy$$

$$< C q^{-\frac{2}{3}} n^{\frac{5}{3}} + C q^{-\frac{2}{3}} n^{\frac{5}{3}} = C q^{-\frac{2}{3}} n^{\frac{5}{3}}.$$

$$\sum_{\mathfrak{M}_1''} \int_{\mathfrak{M}_1''} |\psi_\rho^4(x)|^2 |dx| < C n^{\frac{5}{3}} \sum_{q > n^{\delta a}} q^{-\frac{2}{3}+1}$$

$$< C n^{\frac{5}{9} - \frac{2}{3}\delta a}$$

Hence,

$$\int_C |f^4(x) - \sum_{q \leqslant n^{\delta a}} \psi_\rho^4(x)|^2 \, |dx|$$

$$< Cn^{\frac{5}{3}} \left\{ n^{3\epsilon_1 - \epsilon_2 + \epsilon} + n^{-\epsilon_1\theta + 10\epsilon} + n^{-\frac{1}{9}} + n^{-\frac{2}{3}\delta a} \right\}$$

$$= Cn^{\frac{5}{3}} \left\{ n^{3\epsilon_1 - \epsilon_2 + \epsilon} + n^{-\epsilon_1\theta + 10\epsilon} + n^{-\frac{1}{9}} + n^{-\frac{1}{12}} \right\}$$

The right side is $0\ (n^{\frac{5}{3}})$ because all the exponents of n in the four terms occurring in the brackets are negative since we choose ϵ_1 and ϵ_2 (arbitrarily small and positive) in such a way that $\epsilon_2 > 3\epsilon_1$, and ϵ is arbitrarily small.

THEOREM 17. *If*

$$\sum_1^x g^2(n) = 0(x^{\frac{5}{3}}) \tag{1}$$

then

$$g(n) = 0\ (n^{\frac{1}{3}})$$

for almost all n.

Proof: We first show that

(C): the set of n's for which

$$g(n) \neq 0\ (n^{\frac{1}{3}})$$

has zero density.

For if the set of n's for which

(D): $$|g(n)| > cn^{\frac{1}{3}} \qquad (c > 0)$$

has positive density λ, then (D) is true for the p values of $n \leqslant x$,

$$n = x_1, \cdots, x_p$$

where $$\lim_{x \to \infty} \frac{p}{x} \geqslant \lambda$$

whence $$\sum_{n=1}^x |g^2(n)| > c^2 (x_1^{\frac{2}{3}} + \cdots + x_p^{\frac{2}{3}})$$

$$> c^2 (1^{\frac{2}{3}} + 2^{\frac{2}{3}} + \cdots + p^{\frac{2}{3}}) \sim \frac{c^2 p^{\frac{5}{3}}}{\frac{5}{3}}$$

$$> \frac{3c^2}{5} (\lambda - \epsilon)^{\frac{5}{3}} x^{\frac{5}{3}} > \frac{3c^2}{5} \left(\frac{\lambda}{2}\right)^{\frac{5}{3}} x^{\frac{5}{3}}$$

which contradicts (1).

This proves (C). Hence the set of n's for which

$$g(n) = 0\ (n^{\frac{1}{3}}) \tag{2}$$

has density 1, *i.e.*, (2) is true for almost all n.

The Concluding Argument.

THEOREM 18. *Put*

$$\sigma(j) = r_4(j) - \Gamma^3(\tfrac{4}{3}) \frac{\Gamma(\frac{4}{3}+j)}{j!} \mathrm{S}(j, n^{\delta a})$$

Then

$$\sum_{j=1}^{n} |\sigma(j)|^2 = 0(n^{\frac{5}{3}})$$

Proof: We have

$$\psi_\rho(x) = \left\{1 + \sum_{j=0}^{n} \frac{a(a+1)\cdots(a+j-1)}{j!}\left(\frac{x}{\rho}\right)^j\right\} \Gamma(\tfrac{4}{3}) \frac{\mathrm{S}_\rho}{q}$$

$$\phi_\rho(x) = \left\{\sum_{j=n+1}^{\infty} \frac{a(a+1)\cdots(a+j-1)}{j!}\left(\frac{x}{\rho}\right)^j\right\} \Gamma(\tfrac{4}{3}) \frac{\mathrm{S}_\rho}{q}$$

$$\mathrm{W}_\rho(x) = \psi_\rho(x) + \phi_\rho(x) = \Gamma(\tfrac{4}{3}) \frac{\mathrm{S}_\rho}{q}\left(1 - \frac{x}{\rho}\right)^{-a}$$

Hence

$$\{\mathrm{W}_\rho(x)\}^4 = \Gamma^4(\tfrac{4}{3}) \left(\frac{\mathrm{S}_\rho}{q}\right)^4 \left(1 - \frac{x}{\rho}\right)^{-\frac{4}{3}} \tag{3}$$

Now the terms upto x^n in $\psi_\rho{}^4(x)$ must be the same as the terms upto x^n in $\{\mathrm{W}_\rho(x)\}^4$

Hence from (3)

$$\psi_\rho{}^4(x) = \Gamma^4(\tfrac{4}{3}) \left(\frac{\mathrm{S}_\rho}{q}\right)^4 \left\{1 + \sum_{j=1}^{n} \frac{\frac{4}{3}(\frac{4}{3}+1)\cdots(\frac{4}{3}+j-1)}{j!}\left(\frac{x}{\rho}\right)^j\right\}$$

$$+ \text{ other terms upto } x^{4n}.$$

$$= \Gamma^3(\tfrac{4}{3}) \left(\frac{\mathrm{S}_\rho}{q}\right)^4 \left\{\Gamma(\tfrac{4}{3}) + \sum_{j=1}^{n} \frac{\Gamma(\frac{4}{3}+j)}{j!}\left(\frac{x}{\rho}\right)^j\right\} \tag{4}$$

$$+ \text{ terms upto } x^{4n}.$$

Again

$$f(x) = \sum_{h=0}^{n^{\frac{4}{3}}} x^{h^3}$$

so that

$$f^4(x) = 1 + \sum_{j=1}^{n} r_4(j)x^j + \text{terms upto } x^{4n} \text{ at most.} \tag{5}$$

From (4) and (5) we get

$$f^4(x) - \sum_{q=1}^{n^{\delta a}} \psi_\rho{}^4(x)$$

$$= c_0 + \sum_{j=1}^{n} x^j \left\{r_4(j) - \Gamma^3(\tfrac{4}{3}) \frac{\Gamma(\frac{4}{3}+j)}{j!} \sum_{q=1}^{n^{\delta a}} \left(\frac{\mathrm{S}_\rho}{q}\right)^4 \rho^{-j}\right\}$$

$$+ \text{ terms in } x^j \ (n+1 \leqslant j \leqslant 4n)$$

where c_0 is independent of x.

Change x into $e^{2\pi iy}$. Then

$$f^4(e^{2\pi iy}) - \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(e^{2\pi iy})$$

$$= c_0 + \sum_{j=1}^{n} e^{2\pi iyj}\left\{r_4(j) - \Gamma^3(\tfrac{4}{3})\frac{\Gamma(\frac{4}{3}+j)}{j!}\sum_{q=1}^{n^{\delta a}}\left(\frac{S_\rho}{q}\right)^4 \rho^{-j}\right\}$$

$+$ terms in $e^{2\pi iyj}$ where j goes from $n+1$ upto $4n$

$$= c_0 + \sum_{j=1}^{n} e^{2\pi iy}\,\sigma(j) + \text{terms in } e^{2\pi iyj}\ (n+1 \leqslant j \leqslant 4n)$$

where c_0 is independent of y.

Hence from Theorem 2 it follows that

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} |f^4(e^{2\pi iy}) - \sum_{q=1}^{n^{\delta a}} \psi_\rho^4(e^{2\pi iy})|^2\, dy$$

$$\geqslant \sum_{j=1}^{n} |\sigma(j)|^2. \tag{6}$$

But by Theorem 16 the left side of (6) is $0(n^{\frac{5}{3}})$. Hence so is the right side of (6). Since

$$\sum_{j=1}^{n} |\sigma(j)|^2 = 0(n^{\frac{5}{3}})$$

it follows by Theorem 17 that

$$\sigma(j) = 0(j^{\frac{1}{3}})$$

for almost all j. Hence

$$r_4(j) - \Gamma^3(\tfrac{4}{3})\frac{\Gamma(\frac{4}{3}+j)}{j!}\,S(j, n^{\delta a})$$

$$= 0(j^{\frac{1}{3}}) \quad \text{for almost all } j. \tag{7}$$

Now

$$\Gamma^3(\tfrac{4}{3}) > 0 \text{ for } \Gamma(\tfrac{4}{3}) = \int_0^\infty e^{-x} x^{\frac{1}{3}}\, dx > 0$$

and

$$\frac{\Gamma(\frac{4}{3}+j)}{j!} \sim j^{\frac{1}{3}} \text{ (by Theorem 3)}$$

also

$$S(j, n^{\delta a}) = \sum_{q=1}^{n^{\delta a}} A(q, j)$$

$$= \sum_{q=1}^{\infty} A(q, j) - \sum_{q > n^{\delta a}} A(q, j)$$

$$= c(j) - \sum_{q > n^{\delta a}} A(q, j) \tag{8}$$

where $c(j)$ is greater than a certain absolute positive constant c (Lemma 2 of P. N. VI). Again (by Lemma 5 of P. N. VI)

$$\sum_{q > m} A(q, j) = O\left(m^{-f} [d(j)]^3\right) \tag{9}$$

where f is an absolute positive constant and $d(n)$ denotes the number of divisors of n.

From (9)

$$\sum_{q > n^{\delta a}} A(q, j) = \frac{O(j^{\epsilon})}{n^{f\delta a}} = \frac{O(n^{\epsilon})}{n^{f\delta a}} \to 0 \tag{10}$$

as $n \to \infty$

since $j \leqslant n$.

From (8) and (10)

$$S(j, n^{\delta a}) > \frac{c}{2} \text{ as } n \to \infty. \tag{11}$$

From (7) and (11)

$$r_4(j) > Dj^{\frac{1}{3}} \tag{12}$$

for almost all j, where D is an absolute positive constant. Hence our result.

RAMAN SPECTRUM OF BENZENE VAPOUR.

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1. Introduction.

The distribution of intensity within the wing accompanying the Rayleigh lines in liquids in general and benzene in particular has beeen investigated by Gerlach (1929), Weiler (1931), Ranganadham (1932), Bhagavantam and Veerabhadra Rao (1934), Bhagavantam (1935), Rousset (1935) and others. All these authors have expressed the view that the experimentally observed distribution of intensity is very different from that which is to be expected if the usual laws which are strictly applicable only to gases are also applicable to liquids. The chief point of difference lies in the fact that while the wings accompanying the Rayleigh lines in gases show a maximum of intensity which is well separated from the central peak, no such phenomenon has been noticed in liquids. The maximum appears to merge into the central peak. Contrary to the findings of the above authors, Sirkar and Maiti (1935) have reported that the wing in liquid benzene also shows a maximum of intensity separated from the centre to the expected extent. The process adopted by these authors for obtaining the results is somewhat indirect and involves a subtraction of the effects due to the broadening of the centre itself from the observed intensities. Repeated efforts to reproduce their results using instruments of higher dispersion where such a doubtful procedure is altogether eliminated (Bhagavantam, 1935) have not proved successful. In this paper a direct demonstration of the essential difference between the wings in liquid benzene and the wings in benzene vapour is furnished. A high dispersion instrument is used to photograph the liquid wings alongside the vapour wings under identical conditions. Microphotometric records (Fig. 2) as well as visual observation of the plates clearly show that a particular dispersion of the instrument, conditions of observation, intensity of exposure, etc., which are carefully selected to show up the maximum of intensity very distinctly separated from the centre in the vapour state, do not show any such thing in the liquid. On the other hand, the distribution of intensity in the liquid is wholly different from that observed in the vapour

inasmuch as there is a greater concentration towards the centre. The present investigation has been taken up with a view to clear up this and other related features which will be discussed in detail in the following sections.

Much interest also attaches to the structure of benzene and a series of important papers by Angus and others (1936) dealing with this subject have recently appeared in the *Journal of the Chemical Society*. Comparison of Raman, infra-red and emission spectra of benzene with those of deutero-benzenes is one of the main themes of the above papers. In this connection, a detailed knowledge of the Raman spectrum of benzene vapour appears to be very desirable. The present paper is also an attempt in this direction.

2. *Experimental Arrangements.*

A small quantity of benzene is contained in a thick wall pyrex glass tube which is sealed up after exhaustion. The tube is maintained at a temperature of about 180° C. by means of a suitably constructed electric furnace during the exposure. Under these conditions, benzene vapour is in equilibrium with its own liquid at a pressure of about 15 atmospheres. The rest of the arrangements are similar to those that are ordinarily employed for the study of Raman spectra. Condenser method of illumination is used and a 2-prism glass spectrograph employed for the photographing of the Raman spectra. The Raman spectrum of the vapour is recorded through a Hartmann diaphragm. The vapour tube is removed and a liquid tube inserted and the time of exposure reduced correspondingly so as to get pictures of comparable intensity and the spectrum of the liquid is recorded on either side of the vapour picture under identical conditions of slit width, illumination, etc.

A Moll microphotometer has been used to obtain photometric records of the rotation wings accompanying the Rayleigh lines.

3. *Results.*

The following are the main features noticed in the present investigation. Items 1 to 4 relate to the vibration lines and items 5 to 7 relate to the rotational wings.

1. The principal Raman line 992 shows no shift as we pass from liquid to vapour (see Fig. 1).

2. The Raman line at 600 shows no shift as we pass from liquid to vapour.

3. The Raman line at 3061 in the liquid shows a definite shift as we pass to the vapour state (see Fig. 1). In the latter case it has a value of 3069.

4. The Raman line at 3047 has either completely disappeared or has been considerably weakened (see Fig. 1). Examination of the original negatives shows only a suspicious trace of this line in the vapour.

5. The rotation wings accompanying the Rayleigh lines in the liquid show no intensity maximum separated from the centre (Fig. 2 *a*) whereas there is a distinct maximum in the case of the vapour lines which may be seen visually in the negatives as also in Fig. 1 and is reproduced in the microphotometric records *b* and *c* of Fig. 2. In this connection it is important to note that the slit width of the spectrograph, the conditions of microphotometring, etc., have been unaltered from the liquid to the vapour and yet the maximum shows up very clearly at the expected place in Fig. 2 *b* and *c* and not so in Fig. 2 *a*. The fact that the time of exposure is relatively large for the vapour is, if any, more unfavourable for the appearance of a separated maximum but it shows up in spite of it. Similarly the much smaller intensity of the wing in Fig. 2 *a* in comparison with that in Fig. 2 *c* is more favourable for showing up the structure of the wing in Fig. 2 *a* but no such thing is noticed in it whereas the flattening is very clearly seen in Fig. 2 *c* in spite of the unfavourable conditions.

6. The distribution of intensity within the wing accompanying the Rayleigh lines in the liquid (Fig. 2 *a*) is altogether different from that obtained in the gas (Fig. 2 *b* and *c*) in that there is a greater concentration of intensity towards the centre in the former case.

7. A new feature which is of very great significance and which has hitherto not been noticed at all is the considerable weakening of the absolute intensity of the wing as we pass from the vapour to the liquid. On comparing Fig. 1 *b* with Fig. 1 *c*, it is easily seen that in the liquid picture, while the 992 Raman line is slightly stronger than that recorded in the gas picture, the wing accompanying the Rayleigh lines is several times weaker. This is best realised on comparing the wings accompanying the 4077 mercury lines.

4. Discussion of Results.

In this connection, we have to refer to the earlier work of Sirkar (1936) on the Raman spectrum of benzene vapour. He has noticed that the line at 3047 broadens and becomes very weak in the vapour. This is in accordance with our observations. The disappearance or the considerable weakening of the line at 3047 in the vapour is, in our opinion, very significant and cannot easily be reconciled with the view expressed by Angus, Bailey and others (1936) that it is a fundamental of the benzene molecule. Our results are however at variance with those reported by Sirkar in one important respect. He observed that the line 3064 remains unshifted from the liquid to the vapour whereas our pictures reproduced in Fig. 1 clearly show the shift.

The other notable features of our investigation relate to the rotation wings. Fig. 2 *a* demonstrates clearly the absence of a separated maximum of intensity in the wings accompanying the Rayleigh lines in liquid benzene while it is easily recorded under identical circumstances in the vapour (Fig. 2 *b* and *c*). This result, which in our opinion is now definitely established, does not involve any particular and detailed process of arriving at the intensity distribution and is therefore free from errors that are likely to arise in the methods adopted by Sirkar and Maiti (1935). The pictures also show clearly a greater concentration of intensity in the case of the liquid at the centre.

The fall in the absolute intensity of the wing noted under item 7 of the section on results, which occurs as we pass from the vapour to the liquid, is very significant. In the case of these wings, there is little doubt that we are dealing with incoherent radiation as in the case of the vibration Raman lines and the passage from the vapour to the liquid state should affect equally the intensities of these two types of scattered radiations and the effect should merely consist in an apparent increase of the intensity caused by the increase in the density of the medium. The coherent or the polarised part of the Rayleigh scattering is however subject to a slightly more complicated law of variation as in this case we have to consider interference effects due to close packing in the liquid. Under these circumstances, one would expect that the intensity of the rotation wings or more correctly the depolarised part of the Rayleigh scattering will bear a definite relationship to that of the vibration Raman line and that this relationship will not depend upon the state of the medium provided the optical anisotropy of the molecule is independent of the state of the medium. The fact that this expectation breaks down to a large degree is a very surprising and entirely new result. The observed facts noted under item 7 of the section on results must mean either that the effective optical anisotropy of the benzene molecules in the liquid state is several times smaller than the corresponding property of the vapour molecules or that the molecules in the liquid are not free to rotate. The first alternative is not in agreement with the conclusions drawn from other branches of light scattering. The second alternative implies no diminution in the total intensity of the incoherent scattering but only means a redistribution between the centre and the wings. If the molecules do not rotate or rotate only partially, the Q branch must gain in intensity at the expense of the P and R branches, the total intensity of the P, Q and R branches which constitute the total incoherent scattering remaining unaltered. This would mean that in liquid benzene, we should not get the full quota of intensity for the rotation wings as would be expected if the gas

laws were applicable. This conclusion is not in agreement with the results of Rousset (1935) who claims to have shown by the method of wide and narrow slits that the total intensity of the P and R branches in liquid benzene is three-fourths the total incoherent scattering. We are investigating liquid benzene and other liquids at different temperatures with a view to throw further light on this problem.

5. Summary.

The Raman spectra of benzene in the liquid and vapour states have been photographed alongside each other under identical conditions of slit width and illumination. While the 600 and 992 Raman lines show no shift, the line at 3061 shifts to 3069 as we pass from the liquid to the vapour. The Raman line at 3047 observed in the liquid has either completely disappeared or considerably weakened in the vapour. The rotation wings accompanying the Rayleigh lines in the liquid show no intensity maximum separated from the centre whereas there is a distinct maximum in the case of the vapour. This result is demonstrated with the help of microphotometric records. The distribution of intensity within the wings in the case of the liquid is very different from that obtained in the case of the vapour. When judged by comparing with the 992 Raman line, a very considerable fall in the absolute intensity of the wings is noticed as we pass from the vapour to the liquid. The significance of this result is discussed.

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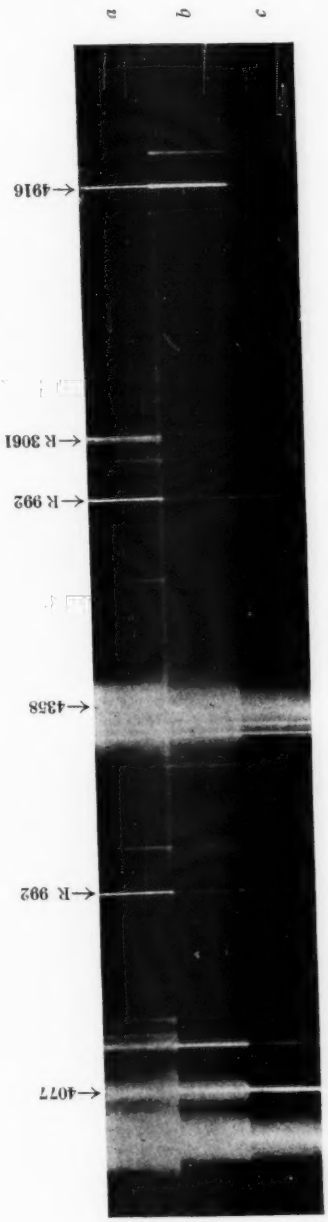

FIG. 1.

a and *c*: Raman spectra of liquid benzene; *b*: Raman spectrum of benzene vapour.

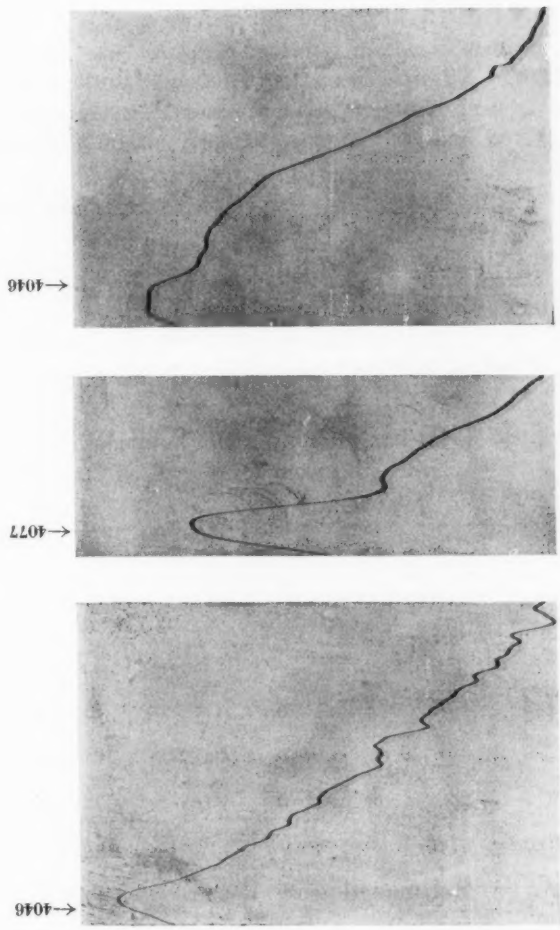

FIG. 2.

a: Wing accompanying the **4046** line in liquid benzene; *b* and *c*: wings accompanying the **4077** and **4046** lines respectively in benzene vapour.

ON THE FLEXURE OF A HOLLOW SHAFT—II.

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In Part I[1] we have given the complete mathematical solution for the flexure of a hollow shaft with a cavity placed excentrically. In the present paper we propose to discuss the amount of twist produced in the asymmetrical case, the value of stress at different points of the section, and the lines of shearing stress.

Our transformation

$$x + iy = c \tan \tfrac{1}{2} (\xi + i\eta)$$

gives

$$x = \frac{c \sin \xi}{\cos \xi + \cosh \eta}, \quad y = \frac{c \sinh \eta}{\cos \xi + \cosh \eta},$$

the boundaries being given by $\eta = \alpha$ and $\eta = \beta$.

In the following numerical calculation we assume $c = 1$, $\alpha = 2$, $\beta = 1$, and $\sigma = \frac{1}{4}$.

The corresponding values of (x, y) and (ξ, η) are given in Table I for a few points of the section for future reference.

Table I.

ξ/π	$\eta = 1$		$\eta = 1{\cdot}5$		$\eta = 2$	
	x	y	x	y	x	y
0	0	0·4621	0	0·6351	0	0·7616
$\frac{1}{4}$	0·3142	0·5223	0·2311	0·6960	0·1582	0·8115
$\frac{1}{3}$	0·4239	0·5752	0·3036	0·7465	0·2031	0·8509
$\frac{1}{2}$	0·6481	0·7616	0·4251	0·9052	0·2658	0·9640
$\frac{5}{8}$	0·7962	1·0128	0·4691	1·0810	0·2734	1·0732
$\frac{3}{4}$	0·8458	1·4055	0·4298	1·2942	0·2314	1·1872
$\frac{5}{6}$	0·7385	1·7359	0·3364	1·4326	0·1726	1·2523
$\frac{7}{8}$	0·6181	1·8979	0·2679	1·4906	0·1348	1·2778
1	0	2·1639	0	1·5750	0	1·3130

[1] Seth, *Proc. Ind. Acad. Sci.*, 1936, **4**, 531–541.

The section is symmetrical about the axis of y, and we have only to change x into $-x$ to get the corresponding values for the other half of the section.

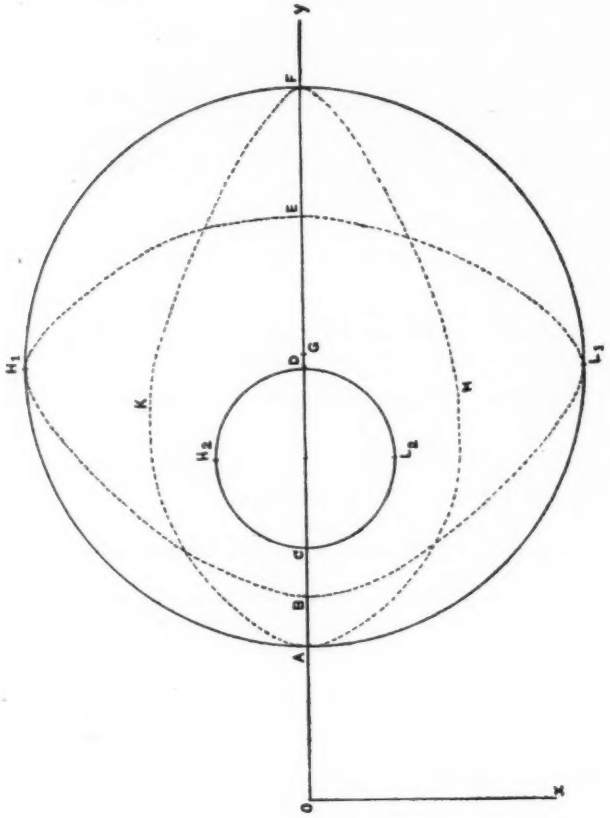

FIG. 1.

1. Asymmetrical Flexure.

In this case the shearing stresses $\widehat{xz}$ and $\widehat{yz}$ can be written as

$$\widehat{xz} = \left(\mu\tau + \sigma\bar{y}\frac{\mu W}{EI}\right)\left(\frac{\partial\Omega}{\partial y} - y\right) + \frac{\mu W}{EI}\left[\tfrac{1}{2}c^3\frac{\partial\psi_2}{\partial y} - \tfrac{1}{4}c^2(3+2\sigma) - \tfrac{1}{4}(3+2\sigma)x^2 - \tfrac{1}{4}(1-2\sigma)y^2\right], \quad (1.1)$$

$$\widehat{yz} = \left(\mu\tau + \sigma\bar{y}\frac{\mu W}{EI}\right)\left(-\frac{\partial\Omega}{\partial x} + x\right) + \frac{\mu W}{EI}\left[-\tfrac{1}{2}c^3\frac{\partial\psi_2}{\partial x} - (\tfrac{1}{2}+\sigma)xy\right], \quad (1.2)$$

where

$$\Omega = 2c^2 \sum_{n=1}^{\infty} \frac{(-1)^n \cos n\xi}{\sinh n(\beta - \alpha)} \Big[e^{-n\beta} \coth \beta \sinh n(\eta - \alpha) + e^{-n\alpha} \coth \alpha \sinh n(\beta - \eta) \Big], \quad (2.1)$$

$$\psi_2 = 2 \sum_{n=1}^{\infty} \frac{(-1)^n \cos n\xi}{\sinh n(\beta - \alpha)} \Big[e^{-n\beta} \coth \beta (n + \coth \beta) \sinh n(\eta - \alpha) + e^{-n\alpha} \coth \alpha (n + \coth \alpha) \sinh n(\beta - \eta) \Big]. \quad (2.2)$$

From (1) we see that the amount of twist per unit length of the shaft about the axis of z through the origin 0 (see Fig. 1) is given by

$$\mathrm{T} = \left(\tau + \sigma \bar{y} \frac{\mathrm{W}}{\mathrm{EI}} \right). \quad (3)$$

The equatuion to determine τ is

$$\begin{aligned} &- \frac{\mu\pi\tau}{\mathrm{W}} \left[\tfrac{1}{2} (b^4 - a^4) + 4c^2k^2 \sum_{n=1}^{\infty} \frac{n e^{-n(\alpha+\beta)}}{\sinh n(\beta - \alpha)} \right] \\ &= \bar{y} + \tfrac{1}{2} \mu\pi \frac{\sigma\bar{y}}{\mathrm{EI}} (b^4 - a^4) - \frac{\mu\pi c}{\mathrm{EI}} (\tfrac{1}{2} + \sigma) (b^4 \coth \beta - a^4 \coth \alpha) \\ &+ \frac{2\mu\pi c^3 k^2}{\mathrm{EI}} \sum_{n=1}^{\infty} \frac{n^2 e^{-n(\alpha+\beta)}}{\sinh n(\beta - \alpha)} \\ &+ \frac{2\mu\pi c^2 k^2}{\mathrm{EI}} [c (\coth \alpha + \coth \beta) + 2\sigma\bar{y}] \sum_{n=1}^{\infty} \frac{n e^{-n(\alpha+\beta)}}{\sinh n(\beta - \alpha)}. \end{aligned} \quad (4)$$

If we take $c = 1$, $\alpha = 2$, $\beta = 1$, $\sigma = \frac{1}{4}$, we get

$$a = 0{\cdot}2757, \quad b = 0{\cdot}8509, \quad \bar{y} = 1{\cdot}3450,$$
$$k^2 = 0{\cdot}0761, \quad \mathrm{I} = \tfrac{1}{4}(0{\cdot}5187)\,\pi,$$

and

$$\left.\begin{aligned} \mu\tau &= (0{\cdot}215) \frac{\mathrm{W}}{\pi}, \\ \mathrm{T} &= (1{\cdot}253) \frac{\mathrm{W}}{\mu\pi}. \end{aligned}\right\} \quad (5.1)$$

Again, if we change the value of α from 2 to 3, we find

$$\left.\begin{aligned} \mu\tau &= (0{\cdot}027) \frac{\mathrm{W}}{\pi}, \\ \mathrm{T} &= (1{\cdot}032) \frac{\mathrm{W}}{\mu\pi}. \end{aligned}\right\} \quad (5.2)$$

To get a numerical idea of τ and T we put $\mathrm{W} = 10$ tons, and $\mu = 8 \times 10^{11}$. Table II shews the corresponding values of τ and T.

TABLE II.

No.	a	b	W in tons	τ in degrees	T in degrees
1	0·2757	0·8509	10	0·05	0·31
2	0·0998	0·8509	10	0·01	0·26
3	0	0·8509	10	0	0·25

As was to be expected τ decreases as the radius a of the inner boundary decreases. In the limiting case when $a = 0$, $\tau = 0$.

Determination of Stress.

To determine $\partial\Omega/\partial x$ and $\partial\Omega/\partial y$ from (2. 1) we have the relations

$$\frac{\partial\Omega}{\partial x}\left[\left(\frac{\partial x}{\partial\xi}\right)^2+\left(\frac{\partial x}{\partial\eta}\right)^2\right] = \frac{\partial\Omega}{\partial\xi}\frac{\partial x}{\partial\xi}+\frac{\partial\Omega}{\partial\eta}\frac{\partial x}{\partial\eta},$$

$$\frac{\partial\Omega}{\partial y}\left[\left(\frac{\partial x}{\partial\xi}\right)^2+\left(\frac{\partial x}{\partial\eta}\right)^2\right] = -\frac{\partial\Omega}{\partial\xi}\frac{\partial x}{\partial\eta}+\frac{\partial\Omega}{\partial\eta}\frac{\partial x}{\partial\xi},$$

which give

$$c\frac{\partial\Omega}{\partial x} = (1+\cos\xi\cosh\eta)\frac{\partial\Omega}{\partial\xi}-\sin\xi\sinh\eta\frac{\partial\Omega}{\partial\eta}, \tag{6. 1}$$

$$c\frac{\partial\Omega}{\partial y} = \sin\xi\sinh\eta\frac{\partial\Omega}{\partial\xi}+(1+\cos\xi\cosh\eta)\frac{\partial\Omega}{\partial\eta}. \tag{6. 2}$$

Similar expressions can be obtained for $\partial\psi_2/\partial x$ and $\partial\psi_2/\partial y$.

On the boundary (2. 1) and (2. 2) become

$$\Omega = \tfrac{1}{2}c^2\left[\frac{2\cosh\eta}{\cos\xi+\cosh\eta}-1\right]+c^2(\tfrac{1}{2}-\coth\eta),$$

$$\psi_2 = \frac{\sinh\eta\cosh\eta}{(\cos\xi+\cosh\eta)^2}-\coth^2\eta,$$

and hence

$$\left(\frac{\partial\Omega}{\partial\xi}\right)_{\eta=\alpha,\beta} = \frac{\sin\xi\cosh\eta}{(\cos\xi+\cosh\eta)^2} = xy\coth\eta, \tag{7. 1}$$

$$\left(\frac{\partial\psi_2}{\partial\xi}\right)_{\eta=\alpha,\beta} = \frac{2\sin\xi\sinh\eta\cosh\eta}{(\cos\xi+\cosh\eta)^3} = 2xy^2\coth\eta. \tag{7. 2}$$

We also find

$$\tfrac{1}{4}\left(\frac{\partial\Omega_2}{\partial\eta}\right)_{\eta=2} = -(0\cdot7944)\sum_{n=1}^{\infty}\frac{n(-1)^n}{e^{2n}-1}\cos n\xi$$

$$+(0\cdot5186)\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-2n}}{e^{2n}-1}\cos n\xi, \tag{7. 3}$$

$$\tfrac{1}{4}\left(\frac{\partial \Omega_2}{\partial \eta}\right)_{\eta=1} = (0\cdot3807)\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-n}}{e^{2n}-1}\cos n\xi$$

$$-(0\cdot6565)\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-n}}{1-e^{-2n}}\cos n\xi, \qquad (7.\ 4)$$

$$\tfrac{1}{4}\left(\frac{\partial \psi_2}{\partial \eta}\right)_{\eta=2} = -\sum_{n=1}^{\infty}\frac{n(-1)^n}{e^{2n}-1}\left[1\cdot1862+0\cdot7944n\right]\cos n\xi$$

$$+\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-2n}}{e^{2n}-1}\left[0\cdot5380+0\cdot5186n\right]\cos n\xi, \qquad (7.\ 5)$$

$$\tfrac{1}{4}\left(\frac{\partial \psi_2}{\partial \eta}\right)_{\eta=1} = \sum_{n=1}^{\infty}\frac{n(-1)^n e^{-n}}{e^{2n}-1}\left[0\cdot2139+0\cdot3807n\right]\cos n\xi$$

$$-\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-n}}{1-e^{-2n}}\left[0\cdot8621+0\cdot6565n\right]\cos n\xi. \qquad (7.\ 6)$$

The value of the stress at any point of the boundary can be obtained with the help of equations (7). Table III gives the stress at some of these points.

For points within the section we have calculated the results for $\eta = 1\cdot5$. In this case the equations corresponding to (7) are

$$\tfrac{1}{2}\left(\frac{\partial \Omega}{\partial \xi}\right)_{\eta=1\cdot5} = (0\cdot2758)\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-\frac{3}{2}n}}{e^n+1}\sin n\xi$$

$$-(1\cdot3130)\sum_{n=1}^{\infty}n(-1)^n e^{-\frac{3}{2}n}\sin n\xi,$$

$$\tfrac{1}{2}\left(\frac{\partial \Omega}{\partial \eta}\right)_{\eta=1\cdot5} = -(0\cdot2758)\sum_{n=1}^{\infty}\frac{n(-1)^n e^{-\frac{3}{2}n}}{e^n-1}\cos n\xi$$

$$-(1\cdot3130)\sum_{n=1}^{\infty}n(-1)^n e^{-\frac{3}{2}n}\cos n\xi,$$

with similar results for $\partial\psi_2/\partial\xi$ and $\partial\psi_2/\partial\eta$.

The values of $\widehat{xz}$ and $\widehat{yz}$ at some points of $\eta = 1\cdot5$ are given in Table III.

To verify that the type of formulæ used in (7) give sufficiently accurate results we can substitute the value, of $\widehat{xz}$ and $\widehat{yz}$ over $\eta = 1$, and $\eta = 2$ in the boundary condition

$$\widehat{xz}\cos(xv) + \widehat{yz}\cos(yv) = 0.$$

The results in Table III satisfy this relation between $\widehat{xz}$ and $\widehat{yz}$.

TABLE III.

$s_1 = \widehat{xz}\mathrm{I}/\mathrm{W}, \quad s_2 = \widehat{yz}\mathrm{I}/\mathrm{W}, \quad \mathrm{S} = (\widehat{xz}^2 + \widehat{yz}^2)^{\frac{1}{2}}\mathrm{I}/\mathrm{W}.$

η	$\xi = 0$			$\xi = \frac{1}{4}\pi$			$\xi = \frac{1}{2}\pi$			$\xi = \frac{3}{4}\pi$			$\xi = \pi$		
	s_1	s_2	S	s_1	s_2	S	s_1	s_2	S	s_1	s_2	S	s_1	s_2	S
1	0·360	0	0·360	0·288	0·115	0·310	0·167	0·196	0·257	0·003	−0·027	0·027	0·223	0	0·223
1·5	0 426	0	0·426	0·294	0·133	0·323	0·147	0·110	0·184	0·169	−0·047	0·175	0·336	0	0·336
2	0·563	0	0·563	0·383	0·268	0·467	0·038	0·138	0·144	0·156	−0·233	0·280	0·567	0	0·567

$\widehat{xz}$ and $\widehat{yz}$ both vanish at the highest and lowest points of $\eta = 1$ and $\eta = 2$.

From Table III we see that on any circle η = constant, the resultant shearing stress decreases from a maximum at $\xi = 0$ to a minimum at some point $\xi = \xi_m$ between $\xi = 0$ and $\xi = \pi$, and then increases to a maximum at $\xi = \pi$. Similar remarks hold good for the other half of the section. On the axis of symmetry it attains a maximum value (0·5670)W/I at a point on the inner boundary nearest the line of loading.

It may be of some interest to compare the shearing stress due to the twisting of the beam about the axis through 0 with that due to bending. If S_t W/I and S_F W/I respectively denote their absolute values we get the following comparison table :

TABLE IV.

η	$\xi = 0$		$\xi = \frac{1}{4}\pi$		$\xi = \frac{1}{2}\pi$		$\xi = \frac{3}{4}\pi$		$\xi = \pi$	
	S_t	S_F	S_t	S_F	S_t	S_F	S_t	S_F	S_t	S_F
1	0·162	0·198	0·154	0·155	0·140	0·118	0·132	0·159	0·132	0·355
1·5	0·145	0·281	0·118	0·190	0·096	0·096	0·061	0·202	0·025	0·361
2	0·152	0·411	0·130	0·337	0·069	0·075	0·012	0·268	0·059	0·508

The maximum value of S_t occurs at $\xi = 0$, $\eta = 1$, which is nearest the axis of twist, and that of S_F occurs at $\xi = \pi$, $\eta = 2$, which is nearest the line of loading. It may be remarked that in general we cannot obtain the value of S in Table III by algebraically adding S_t and S_F.

Lines of Shearing Stress.

The boundaries are obviously lines of shearing stress, since the differential equation

$$\frac{dx}{\widehat{xz}} = \frac{dy}{\widehat{yz}}$$

is satisfied at all points on them. $\widehat{xz}$ and $\widehat{yz}$ vanish at the highest and lowest points H_1, H_2, L_1, L_2, of both the boundaries, and it is easily seen that all the lines of shearing stress pass through H_1 and L_1, touch $\eta = 1$ at these points, and cut the axis of y at right angles. An accurate determination of these lines involves very heavy arithmetic, and, as the values of $\widehat{xz}$ and $\widehat{yz}$ can be more easily obtained at any given point, no attempt at their accurate drawing has been made. From the results we have already obtained their general form may be seen to be that represented by the dotted line BH_1EL_1 in Fig. 1.

2. Symmetrical Flexure.

In this case we find

$$\widehat{xz} = \frac{\mu W}{EI}\left[\frac{\partial \chi_2}{\partial x} + (1+\sigma)\, x\bar{y} - 2\sigma xy\right] \tag{8.1}$$

$$\widehat{yz} = \frac{\mu W}{EI}\left[\frac{\partial \chi_2}{\partial y} + (1+\sigma)\, y\bar{y} - y^2\right] \tag{8.2}$$

where

$$\chi_2 = -2(1+\sigma)\sum_{n=1}^{\infty}\frac{(-1)^n \cos n\xi}{\sinh n(\beta-\alpha)}\Big[(e^{-n\beta}-1)(\coth\beta-\bar{y})\times$$

$$\times \operatorname{cosech}^2\beta \cosh n(\eta-\alpha) - (e^{-n\alpha}-1)(\coth\alpha-\bar{y})\operatorname{cosech}^2\alpha\cosh n(\beta-\eta)\Big]$$

$$+2(1+\sigma)\sum_{n=1}^{\infty}\frac{(-1)^n\cos n\xi}{\sinh n(\beta-\alpha)}\Big[e^{-n\beta}\left(\tfrac{2}{3}+\bar{y}\coth\beta-\coth^2\beta\right)\times$$

$$\times\cosh n(\eta-\alpha) - e^{-n\alpha}\left(\tfrac{2}{3}+\bar{y}\coth\alpha-\coth^2\alpha\right)\cosh n(\beta-\eta)\Big]$$

$$-\sum_{n=1}^{\infty}\frac{(-1)^n n\cos n\xi}{\sinh n(\beta-\alpha)}\Big[e^{-n\beta}\coth\beta\cosh n(\eta-\alpha)$$

$$-e^{-n\alpha}\coth\alpha\cosh n(\beta-\eta)\Big]$$

$$-\tfrac{1}{3}(1-2\sigma)\sum_{n=1}^{\infty}\frac{(-1)^n n^2\cos n\xi}{\sinh n(\beta-\alpha)}\Big[e^{-n\beta}\cosh n(\eta-\alpha)$$

$$-e^{-n\alpha}\cosh n(\beta-\eta)\Big]. \tag{9}$$

Over the boundaries we find

$$\left(\frac{\partial\chi_2}{\partial\eta}\right)_{\eta=\alpha,\beta} = -\left[\frac{(1\cdot6813)\cos\xi\cosh\eta}{(\cos\xi+\cosh\eta)^2}+\frac{\sinh^2\eta(\frac{1}{2}\sin^2\xi-1-\cos\xi\cosh\eta)}{(\cos\xi+\cosh\eta)^4}\right]$$

$$= -[(1\cdot6813)\,xy\cot\xi + \tfrac{1}{2}x^2y^2 - x^2y^2\operatorname{cosec}^2\xi$$

$$-x^2y^2\cot\xi\operatorname{cosec}\xi\cosh\eta], \tag{10.1}$$

$$\tfrac{1}{3}\left(\frac{\partial\chi_2}{\partial\xi}\right)_{\eta=1} = (0\cdot0116)[(0\cdot3130)\sin\xi + (0\cdot4814)\sin 2\xi - (0\cdot6650)\sin 3\xi$$

$$+(0\cdot7498)\sin 4\xi - (0\cdot8000)\sin 5\xi + \tfrac{1}{2}\tan\tfrac{1}{2}\xi]$$

$$-\sum_{n=1}^{\infty}\frac{(-1)^n e^{-n}\sin n\xi}{e^{2n}-1}\left[0\cdot0116+0\cdot6314\,n-0\cdot1523\,n^2\right]$$

$$+\sum_{n=1}^{\infty}\frac{(-1)^n e^{-n}\sin n\xi}{1-e^{-2n}}\left[0\cdot0348+0\cdot3543\,n-0\cdot2626\,n^2\right]$$

$$+\tfrac{1}{30}(\tfrac{1}{2}xy - 3xy^2\coth 1 + 3xy^3), \tag{10.2}$$

$$\tfrac{1}{4}\left(\frac{\partial \chi_2}{\partial \xi}\right)_{\eta=2} = (0\cdot0232)\sum_{n=1}^{\infty}(-1)^n \sin n\xi\left[\frac{1}{e^{2n}-1} - \frac{e^{-n}}{1-e^{-2n}}\right]$$

$$- \tfrac{1}{2}(0\cdot0116)\tan\tfrac{1}{2}\xi + (0\cdot0116)\sum_{n=1}^{\infty}(-1)^n e^{-2n}\sin n\xi$$

$$+ \sum_{n=1}^{\infty}\frac{(-1)^n n \sin n\xi}{e^{2n}-1}\left[0\cdot2156 - 0\cdot3178\, n\right]$$

$$- \sum_{n=1}^{\infty}\frac{(-1)^n n\, e^{-2n}\sin n\xi}{e^{2n}-1}\left[0\cdot4929 - 0\cdot2074\, n\right]$$

$$+ \tfrac{1}{30}\left[\tfrac{1}{2}xy - 3xy^2\coth 2 + 3xy^3\right]. \qquad (10.\ 3)$$

Both (10. 2) and (10. 3) do not hold good for $\xi = \pi$ where $\partial\chi_2/\partial\xi$ vanishes.

In Table V we have given the values of the shearing stress components for a few points of the boundary, and for a few points of $\eta = 1\cdot5$.

TABLE V.

$s_1 = \widehat{xz}$ I/W, $s_2 = \widehat{yz}$ I/W, $S = (\widehat{xz}^2 + \widehat{yz}^2)^{\frac{1}{2}}$ I/W.

η	$\xi = \frac{1}{4}\pi$			$\xi = \frac{1}{2}\pi$			$\xi = \frac{3}{4}\pi$		
	s_1	s_2	S	s_1	s_2	S	s_1	s_2	S
1	0·153	0·061	0·164	0·141	0·166	0·218	− 0·026	0·239	0·240
1·5	0·137	0·080	0·150	0·096	0·280	0·296	− 0·044	0·290	0·294
2	0·205	0·144	0·250	0·115	0·415	0·431	− 0·161	0·248	0·295

Both at $\xi = 0$ and $\xi = \pi$, S vanishes over $\eta = 1$ and $\eta = 2$. The maximum stress occurs near the highest point of the inner boundary ($\eta = 2$), where its value is 0·451 W/I.

Lines of Shearing Stress.

The boundaries are again lines of shearing stress. These lines are symmetrical about the y-axis. They all pass through the points A and F (see Fig. 1) where they touch the circle $\eta = 1$. Their general form is roughly shewn by the curve AKFM in Fig. 1.

A NOTE ON THE MIXED TENSOR T_μ^ν.

By V. V. Narlikar.

(*From the Benares Hindu University.*)

Received September 9, 1936.

The object of this note is to prove two elementary but important properties of T_μ^ν which, as far as the author knows, have not been noticed by relativists. The theorems hold good for n co-ordinates but, for the sake of demonstration, it is sufficient to have three co-ordinates for exploring space and the fourth for marking time.

The first theorem arises out of the question: when do the components of T_μ^ν remain unchanged under a perfectly general Gaussian transformation of co-ordinates? That is, in the usual notation, if

$$T_\mu'^\nu = T_\alpha^\beta \frac{\partial x'^\nu}{\partial x^\beta} \cdot \frac{\partial x^\alpha}{\partial x'^\mu}, \tag{1}$$

we have to find what must be the set of conditions fulfilled so that

$$T_\alpha'^\beta = T_\alpha^\beta \tag{2}$$

From (1) and (2) we get sixteen homogeneous linear equations. The determinant of these equations can be shown to vanish by virtue of the relations

$$\sum_{\alpha=1}^{4} \frac{\partial x'^\nu}{\partial x^\alpha} \cdot \frac{\partial x^\alpha}{\partial x'^\mu} = \delta_\mu^\nu \tag{3}$$

Hence, the sixteen equations form a consistent set, and we have on solving them that

$$T_1^1 = T_2^2 = T_3^3 = T_4^4 \tag{4}$$

$$T_\mu^\nu = 0, \mu \neq \nu \tag{5}$$

Thus, we obtain the theorem that the only tensor T_μ^ν whose components are invariant under a Gaussian transformation is given by

$$T_\mu^\nu = \lambda g_\mu^\nu = \lambda \delta_\mu^\nu, \tag{6}$$

λ being any arbitrary function. When T_μ^ν represents the material energy tensor T_1^1, T_2^2, T_3^3 and T_4^4 do not all have the same sign; so the material energy tensor cannot be of the form (6) except for the trivial case $\lambda = 0$. This last condition means absence of matter. The first theorem thus explains why isotropy in space-time is possible only in the absence of matter as in de Sitter's universe.

For the investigation of spatial isotropy we may proceed by finding the components of $T_\mu{}^\nu$ which remain unchanged when space co-ordinates are transformed into space co-ordinates and the time co-ordinates into another time co-ordinate. We have now

$$\frac{\partial x'^4}{\partial x^4} \neq 0, \quad \sum_{\alpha=1}^{3} \frac{\partial x'^\beta}{\partial x^\alpha} \cdot \frac{\partial x^\alpha}{\partial x'^\gamma} = \partial_\gamma{}^\beta \tag{7}$$

if $\beta, \gamma = 1, 2, 3$. Using (7) as supplementary to (3) we have from the homogeneous equations for $T_\mu{}^\nu$ that

$$T_1{}^1 = T_2{}^2 = T_3{}^3, \; T_\mu{}^\nu = 0, \quad \mu \neq \nu. \tag{8}$$

Thus only the four principal components of $T_\mu{}^\nu$ may be non-zero of which the first three have to be equal. The restrictions (7) are precisely those which characterize the isotropy of an instantaneous cross-section of a space-time field. This theorem giving the well-known conditions of spatial isotropy, *viz.*, (8) from a set of homogeneous equations of transformation seems to be new, at least, in view of Dingle's discussion of isotropy.[1]

When $T_\mu{}^\nu$ represents the material energy of a perfect fluid devoid of mass-motion, conditions (8) are fulfilled. In the general case, however, if there is preferential motion of matter relative to the observer the instantaneous cross-section of space-time cannot be isotropic. Walker[2] has however given a generalised condition of a fluid in motion, called by him a generalised condition of isotropy. This condition really indicates how spatial isotropy is destroyed by the existence of motion and has therefore been excluded from the generality of (8).

Summary.

Two new theorems of relativistic interest regarding $T_\mu{}^\nu$ are given.

[1] Dingle has discussed in the *M. N. R. A. S.*, Dec. 1933, pp. 138-140, permissible, changes of co-ordinates so that the conditions (8) are preserved. This discussion clearly shows that our theorem which gives (8) from a set of equations is unknown to him.

[2] In the *Quarterly J. of Maths. (Oxford)*, June 1935, p. 81, A. G. Walker gives a generalised condition of isotropy for radial motion of a fluid. This condition has been explored by the author and Mr. Moghe in the *M. N. R. A. S.*, Jan. 1935 and the *Phil. Mag.*, Dec. 1935.

ON THE DIFFERENTIAL EQUATION OF THE INSTABILITY OF A THIN LAYER OF FLUID HEATED FROM BELOW.

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and

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The problem of the stability of a thin layer of fluid heated from below has been considered by various authors. The late Lord Rayleigh[1] applied Boussinesq's equations to explain Benard's results. The conclusions were, however, restricted in scope as the equations were solved for a very special boundary case. Jeffreys[2] derived a sixth order differential equation of form

$$(d^2/dx^2 - a^2)^3 y = -\lambda a^2 y$$

on whose solution the discussion of the problem could be based and he attempted to solve the equation by the method of finite differences. Later,[3] in trying to improve the calculation, he found that the assumption of a sine series for y in terms of multiples of πx did not allow the coefficients to be determined and he assigned the failure of the method to the divergence of the derivatives of y when obtained by differentiating more than twice the original series term by term. However, he solved the equations by assuming a sine series for d^6y/dx^6. Low[4] solved the same equation directly in terms of exponential functions. This was possible as the equation (in D)

$$(D^2 - a^2)^3 + \lambda a^2 = 0$$

can be factorised easily. The last method is restricted in scope by its very nature and the earlier method appears somewhat artificial. While attempting to solve more general equations of stability, it was found necessary to employ a general but direct method[5] free from the above restrictions. The application of this method to the differential equation quoted above would be perhaps of sufficient interest to merit publication.

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[1] *Phil. Mag.*, 1916, **32**, 529.

[2] *Ibid.*, 1926, **2**, 833.

[3] *Proc. Roy. Soc.*, 1928, **118**, 195.

[4] *Ibid.*, 1929, **125**, 180.

[5] This method and its application in general will be published shortly.

The equation may be slightly generalised and solved in the form

$$(d^2/dx^2 - a^2)\,(d^2/dx^2 - b^2)\,(d^2/dx^2 - c^2)\,y = -\lambda a^2 y \qquad (1)$$

Let it be assumed that in the interval $0 < x < \pi$

$$y = \sum_1^\infty A_n \sin nx \qquad (2)$$

Then the equation may be written as

$$(d^2/dx^2 - a^2)\,(d^2/dx^2 - b^2)\,(d^2/dx^2 - c^2)\,y = -\lambda a^2 \sum_1^\infty A_n \sin nx \qquad (3)$$

The complete solution of this equation is

$$\begin{aligned} y = {} & B_0 \cosh a\left(\frac{\pi}{2} - x\right) + B_1 \sinh a\left(\frac{\pi}{2} - x\right) \\ & + C_0 \cosh b\left(\frac{\pi}{2} - x\right) + C_1 \sinh b\left(\frac{\pi}{2} - x\right) \\ & + D_0 \cosh c\left(\frac{\pi}{2} - x\right) + D_1 \sinh c\left(\frac{\pi}{2} - x\right) \\ & + \lambda a^2 \Sigma \frac{A_n \sin nx}{(n^2 + a^2)\,(n^2 + b^2)\,(n^2 + c^2)} \end{aligned} \qquad (4)$$

As

$$\frac{2}{\pi}\int_0^\pi \cosh a\left(\frac{\pi}{2} - x\right) \sin nx\, dx = \frac{4n}{\pi}\,\frac{\cosh a\,\pi/2}{n^2 + a^2}\,\sin^2 n\,\pi/2$$

and

$$\frac{2}{\pi}\int_0^\pi \sinh a\left(\frac{\pi}{2} - x\right) \sin nx\, dx = \frac{4n}{\pi}\,\frac{\sinh a\,\pi/2}{n^2 + a^2}\cos^2 n\,\pi/2$$

It follows from a comparison of (2) and (4) that

$$\begin{aligned} & \frac{4n}{\pi}\left(B_0 \cosh a\frac{\pi}{2} + C_0 \cosh b\frac{\pi}{2} + D_0 \cosh c\frac{\pi}{2}\right)\frac{\sin^2 n\,\pi/2}{n^2 + a^2} \\ & + \frac{4n}{\pi}\left(B_1 \sinh a\frac{\pi}{2} + C_1 \sinh b\frac{\pi}{2} + D_1 \sinh c\frac{\pi}{2}\right)\frac{\cos^2 n\,\pi/2}{n^2 + a^2} \\ & = A_n\,[1 - \lambda a^2/(n^2 + a^2)\,(n^2 + b^2)\,(n^2 + c^2)] \end{aligned} \qquad (5)$$

It is evident that A_{2n+1} is dependent only on B_0, C_0 and D_0 while A_{2n} is dependent only on B_1, C_1 and D_1. y can be split up into two parts in one of which x can be replaced by $(\pi\text{-}x)$ without changing its value; while in the other such a replacement changes the algebraic sign only. The two parts may be denoted by y_1 and y_2 and are called "even and odd" solutions

respectively and these two parts can be considered independent of one another if the boundary conditions are similar at $x = 0$ and $x = \pi$.

$$y_1 = B_0 \cosh a\left(\frac{\pi}{2} - x\right) + C_0 \cosh b\left(\frac{\pi}{2} - x\right) + D_0 \cosh c\left(\frac{\pi}{2} - x\right)$$
$$+ \lambda a^2 \sum_{n=0}^{\infty} \frac{A_{2n+1} \sin (2n + 1)\, x}{(2n+1^2 + a^2)\,(2n+1^2 + b^2)\,(2n+1^2 + c^2)}$$

$$y_2 = B_1 \sinh a\left(\frac{\pi}{2} - x\right) + C_1 \sinh b\left(\frac{\pi}{2} - x\right) + D_1 \sinh c\left(\frac{\pi}{2} - x\right)$$
$$+ \lambda a^2 \sum_{1}^{\infty} \frac{A_{2n} \sin 2\, nx)}{(4n^2 + a^2)\,(4n^2 + b^2)\,(4n^2 + c^2)}.$$

If d^4y/dx^4, d^2y/dx^2, $y = 0$ at $x = 0$ and $x = \pi$

$B_0 = C_0 = D_0 = 0$ or $B_1 = C_1 = D_1 = 0$

leading to $A_n = 0$ for all values of n

unless $(n^2 + a^2)\,(n^2 + b^2)\,(n^2 + c^2) = \lambda a^2$

for some value of n. The minimum root for λa^2

is $\lambda a^2 = (1 + a^2)\,(1 + b^2)\,(1 + c^2)$

which occurs in the even solutions.

If $y = 0$, $d^2y/dx^2 = 0$

and $d^3y/dx^3 - k^2 dy/dx = 0$ at $x = 0$

and at $x = \pi$ it follows that

$$\frac{B_0 \cosh a\,\pi/2}{b^2 - c^2} = \frac{C_0 \cosh b\,\pi/2}{c^2 - a^2} = \frac{D_0 \cosh c\,\pi/2}{a^2 - b^2} = L$$

and hence

$$L\,\{a\,(a^2 - k^2)\,(b^2 - c^2) \tanh a\,\pi/2 + b\,(b^2 - k^2)\,(c^2 - a^2) \tanh b\,\pi/2$$
$$+ c(c^2 - k^2)\,(a^2 - b^2) \tanh c\,\pi/2\}$$
$$+ \lambda a^2 \Sigma \frac{A_{2n+1}\,(2n + 1)\,(2n+1^2 + k^2)}{(2n+1^2 + a^2)\,(2n+1^2 + b^2)\,(2n+1^2 + c^2)} = 0.$$

This equation, when $a^2 = b^2 = c^2 = k$,

reduces to the consistency equation given by Jeffreys under similar boundary conditions (*Proc. Roy. Soc.*, **118**, p. 200 *et. seq.*). The odd solution gives a higher value for λa^2 and its treatment would be similar.

A THEOREM OF ERDÖS.

By S. Chowla.

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Received November 21, 1936.

1. Erdös has proved the beautiful result (*Quart. Jour. of Maths.*, Oxford, Sept. 1936) that the no. of solutions of $n = (p-1)(q-1)$ is unbounded, where p, q denote primes. The object of this note is to correct an error in the argument arising from Erdös's citation of a result of Titchmarsh, which was never really proved. The correct form of the result runs as follows :

Let $\pi(x\,;\,k,\,l)$ denote the no. of primes $\equiv l \pmod k$ not exceeding x. Then for all $k \leq \exp(\sqrt{\log x})$, *except possibly for all multiples of a certain number* k_0, we have

$$\pi(x\,;\,k,\,l) = \frac{1}{\phi(k)} \int_2^x \frac{du}{\log u} + O[x \exp(-c\sqrt{\log x})].$$

Here the constant implied in " O " is independent of both x and k. (Titchmarsh, *Rendi. Circ. Mat. Palermo*, 57, 1933, 1—2.)

2. Let p_1 be sufficiently large, $A = p_1 p_2 \cdots p_\lambda$ (a product of λ consecutive primes, choose λ so that

$$(\log A)^2 < p_1 \leqslant \{\log (A p_{\lambda+1})\}^2 < 4 (\log A)^2 \tag{1}$$

(since, by Bertrand's postulate, $p_{\lambda+1} < 2p_\lambda < A$) and $m = [e^{p_1}] + 1$. We evidently have $\exp(\sqrt{\log m}) > A$. Hence we can apply Titchmarsh's theorem above (which we shall refer to as T.) with $x = m$ and $k \leqslant A$ where k/A. Let k_0 (if it exists) be equal to

$$p_{m_1} p_{m_2} \cdots p_{m_r}$$

where the numbers m_s $(1 \leqslant s \leqslant r)$ are all different and each $m_s \leqslant \lambda$. Two cases arise

(a) $$r > \frac{\lambda}{2} + 1.$$

Then T. applies to all combinations of products of the $(r-1)$ different primes

$$p_{m_1}, p_{m_2}, \cdots, p_{m_{r-1}}$$

In this case we define

$$A' = \prod_{s=1}^{r-1} p_{m_s}$$

and observe that T. "*applies*" to all divisors of A′ *in the sense that* none of the divisors of A′ is a multiple of k_0, i.e., *none of the divisors of* A′ *is "exceptional" in the sense of* T.

(β) $r \leqslant \frac{\lambda}{2} + 1$. Then $\left(\frac{A}{k_0}, k_0\right) = 1$ so that if we take $A' = \frac{A}{k_0}$ in this case, we observe that in this case none of the divisors of A′ is "exceptional" in the sense of T.

In both cases, (α) or (β), our definition of A′ ensures that the number of divisors of A′ is at least

$$2^{\frac{1}{2}\lambda - 1}$$

for A′ is a product of at least $\left(\frac{\lambda}{2} - 1\right)$ different primes. Further, since $(A', k_0) = 1$ in one case while $A' < k_0$ in the other, *no divisor of* A′ *is an "exception" when* T. *is applied with* $x = m$, $k \leqslant A'$, k/A'.

We estimate the number of solutions S′ of the congruence

$$(p - 1)(q - 1) \equiv 0 \pmod{A'}$$

with $p, q \leqslant m$.

We write $A' = BC$ and denote by S_B the no. of solutions of

$$(p-1)(q-1) \equiv 0 \pmod{A'},\ p - 1 \equiv 0(B),\ q - 1 \equiv 0(C)$$

with $(q - 1, B) = 1$, $p, q \leqslant m$.

First we estimate S_B.

In virtue of what has been said before, T. applies and hence the no. of solutions of $p - 1 \equiv 0(B)$ with $p \leqslant m$, is greater than $\frac{1}{2} \frac{m}{\phi(B) \log m}$.

Similarly the no. of primes $q \leq m$ for which

$$q - 1 \equiv 0(C) \text{ and } (q - 1, B) = 1$$

is greater than

$$\frac{m}{2\phi(C) \log m} - \sum_{p_i/B} \pi(m ; p_i C, 1)$$

But since $p_i C \leqslant A' \leqslant A < m^{\epsilon}$ it follows from Brun's method that

$$\pi(m ; p_i C, 1) < \frac{c_1 m}{\phi(p_i C) \log m}$$

(c's denoting absolute constants)

Hence

$$\sum_{p_i/B} \pi(m ; p_i C. 1) < \sum_{p_i/B} \frac{c_1 m}{\phi(p_i C) \log m}$$

$$< \frac{c_1 \lambda m}{(p_1 - 1)(\log m)\, \phi(C)} < \frac{c_2 \lambda m}{\phi(C)(\log A)^2 (\log m)}$$

But, from (1), $(\log A)^{2\lambda} < A$ and so $\lambda < \log A$. Thus

$$\sum_{p_i/B} \pi(m ; p_i C, 1) < \frac{c_2 m}{\phi(C)(\log A)(\log m)} < \frac{m}{4\phi(C) \log m}.$$

Hence the no. of primes q such that

$$q - 1 \equiv 0(C), \quad (q-1, B) = 1$$

is greater than $\dfrac{m}{4\phi(C)\log m}$

Hence

$$S_B > \frac{m^2}{8\phi(A')(\log m)^2}$$

We evidently have

$$S' \geqslant \sum_{B/A'} S_B > \frac{2^{\frac{\lambda}{2}-1} m^2}{8A'(\log m)^2}$$

But the integers of the form $(p-1)(q-1)$ with $p, q \leqslant m$ are evidently less than m^2. Hence we may find n ($< m^2$), a multiple of A', for which the equation $n = (p-1)(q-1)$ has more than

$$\frac{2^{\frac{\lambda}{2}-1}}{8\log^2 m} = \frac{2^{\frac{\lambda}{2}}}{16(\log m)^2} \text{ solutions.} \tag{2}$$

But

$$\lambda > \frac{\log A}{3\log\log A}$$

for all prime factors of A are less than $(\log A)^3$ since, by (1), $p_1 < 4(\log A)^2$, and the product of primes in the interval

$$\{4(\log A)^2, (\log A)^3\}$$

is greater than A (this fact follows from the Prime Number Theorem).

Thus since $\log m < 2p_1 < 8(\log A)^2$, we finally have

$$\frac{2^{\frac{\lambda}{2}}}{16(\log m)^2} > \frac{2^{\frac{\log A}{6\log\log A}}}{16.64.(\log A)^4} > \exp[(\log m)^{\frac{1}{2}-\epsilon}]$$

where $\epsilon > 0$ is arbitrary.

Hence for $f(n)$, the no. of solutions of $n = (p-1)(q-1)$ we have,

$$\log f(n) = \Omega\{(\log n)^{\frac{1}{2}-\epsilon}\}$$

where $\epsilon > 0$ is arbitrary, the theorem of Erdös.

3. It is known that if the "extended Riemann hypothesis" is true then, if $(l, k) = 1$, $x \geqslant k^3$,

$$\lim_{k\to\infty} \frac{\pi(x; k, l)}{x/\phi(k)\log x} = 1.$$

Using this fact and $m = A^3$, $A' = A$ in the above argument, we find that if the "extended Riemann hypothesis" is true, then $f(n) \geq \exp\left(\dfrac{c\log n}{\log\log n}\right)$ for some absolute constant $c > 0$, is true for infinitely many n.

ON THE NUMBER OF SOLUTIONS OF SOME CONGRUENCES IN TWO VARIABLES.

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Received December 23, 1936.
(Communicated by Dr. S. Chowla.)

1. *Introduction.*

Hurwitz gave the first proof that the congruence

$$ax^k + by^k \equiv c(p)$$

is soluble with x, y prime to p, whenever $abc \not\equiv 0\ (p)$, for sufficiently large p. This was a generalization of an earlier result due to Dickson. Mordell[1] and Davenport and Hasse[2] proved the stronger result that the number of solutions of the above congruence is asymptotic to p, for large p.

In this paper I give a simple proof of this result by a new method based on lemmas due to Hardy and Littlewood. In fact, I show that

Theorem 1. *If* abc $\not\equiv 0$ (p), *the number* N, *of solutions of*

$$ax^k + by^k + c \equiv 0\ (p^\theta)$$

satisfies the inequality

$$|N - p^\theta| \leqslant (k-1)^2\, p^{\theta - \frac{1}{2}}$$

This is included in the sharper result :

Theorem 2.

$$|N - p^\theta| \leqslant (k-1)(k-2)\, p^{\theta-\frac{1}{2}} + (k-1)\, p^{\theta-1}$$

which is the same as the result due to Davenport and Hasse.

It is not known except in certain special cases whether the congruence

$$y^2 \equiv f(x) \pmod p$$

is soluble where $f(x)$ is a polynomial in x with integral coefficients. But when $f(x) = x^k + c$ it is known from results due to Mordell and Davenport and Hasse that

$$\text{(A)} \qquad \sum_{x=1}^{p} \left(\frac{x^k + c}{p}\right) = 0\ (p)$$

where c is prime to p, and $\left(\frac{n}{p}\right)$ denotes the Legendre symbol of quadratic

[1] *Math. Zeitschr.*, 1933, **37**.
[2] *Crelle's Journal*, 1934, **172**, 151-82.

reciprocity. It seems likely that when $f(x)$ is not congruent (mod p) to a constant multiple of the square of a polynomial in x with integral coefficients, then the number of solutions of

$$y^2 \equiv f(x) \pmod{p}$$

is asymptotic to p, which is equivalent to the result that

$$\sum_{x=1}^{p} \left(\frac{f(x)}{p}\right) \equiv 0 \ (p)$$

In this paper we give a new proof of (A) in the sharper form

Theorem 3.

$$\sum_{x=1}^{p} \left(\frac{x^k + c}{p}\right) = O\left(\sqrt{p}\right)$$

We deduce this as a special case of the result:

Theorem 4. *The number* N, *of solutions of*

$$ax^m + by^n + c \equiv 0 \ (p^\theta) \qquad [abc \not\equiv 0 \ (p)]$$

satisfies

$$|N - p^\theta| \leqslant p^{\theta - \frac{1}{2}} (m_1 - 1)(n_1 - 1)$$

Hence in particular there is always a solution if[3]

$$p > (m_1 - 1)^2 \quad (n_1 - 1)^2$$

where $\qquad m_1 = (m, p-1), \quad n_1 = (n, p-1)$

2. *Notation.*

$$k \geq 2,$$

$S_\rho = \sum_{h=1}^{q} \rho^{h^k}$ where ρ is a primitive qth root of unity, *i.e.*, $\rho = e^{2\pi i \frac{a}{q}}$ where $(a, q) = 1$. $A(q) = A(q, n) = q^{-2} \sum_{\rho} (S_\rho)^2 \rho^{-n}$ where ρ runs over the $\phi(q)$ primitive qth roots of unity.

$M(p^l, n)$ is the number of solutions of $h_1^k + h_2^k \equiv n \ (p^l)$ where $\qquad 0 \leqslant h_1 < p^l, \quad 0 \leqslant h_2 < p^l.$

3. *Proof of Theorem* 1.

Lemma 1.[4]

$$1 + A(p) + \cdots + A(p^l) = p^{-l} M(p^l, n).$$

Lemma 2.[5]

If $p \nmid 2kn$,

$$A(p^l) = 0 \quad \text{for } l > 1.$$

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[3] This is sharper than Mordell's result (*loc. cit.*).

[4] E. Landau, *Vorlesungen über Zahlentheorie*, Band 1, Satz 286. We refer to this book, as LV.

[5] *Ibid.*, Satz 293.

Lemma 3.[6] *If* $p \nmid n$,

$$|A(p)| \leq \frac{(k-1)^2}{\sqrt{p}}$$

We observe that from lemmas 1 to 3 it follows that

$$\left| \frac{M(p^l, n)}{p^l} - 1 \right| \leqslant \frac{(k-1)^2}{\sqrt{p}}$$

i.e., $|N - p^l| \leqslant (k-1)^2 p^{l-\frac{1}{2}}$

which proves Theorem 1 when $a = b = 1$. The generalization is immediate.

4. *Proof of Theorem* 2.

We use the following notation

$$\epsilon = e^{\frac{2\pi i}{p}}$$

and for each character $\chi \pmod p$

$$\tau_\chi = \sum_{l=1}^{p-1} \epsilon^l \chi(l) = \sum_l \epsilon^l \chi(l).$$

and we have (*LV*, satz 308)

$\tau_{\chi_0} = -1$ (where χ_0 is the principal character) $|\tau_\chi| = \sqrt{p}$ $(\chi \neq \chi_0)$.

The $\delta = (k, p-1)$ characters χ with the property $\chi^k = \chi_0$ (*LV*, satz 309) are called " special characters " and will be denoted with the letter $\psi, \psi_0 = \chi_0$. We have (*LV*, satz 310) when $q = p$, $\rho = \epsilon^r$ where $(r, p) = 1$, then

$$S_\rho = \sum_{\psi \neq \psi_0} \psi(r) \tau_{\bar{\psi}}.$$

We have also [*LV*, satz 317)

$$A(p) = p^{-2} \sum_{\psi_1, \psi_2} \tau_{\psi_1} \tau_{\psi_2} \sum_{r=1}^{p-1} e^{\frac{-2\pi i r n}{p}} \bar{\psi}_1(r) \bar{\psi}_2(r)$$

[where ψ_1, ψ_2 run independently over the $\delta - 1$ special characters $\psi \neq \psi_0$]

$$= p^{-2} \left\{ \sum'_{\psi_1, \psi_2} (\ ) + \sum''_{\psi_1, \psi_2} (\ ) \right\}$$

where in Σ' the summation is for ψ_1, ψ_2 subject to $\bar{\psi}_1 \bar{\psi}_2 \neq \chi_0$, and in Σ'' the ψ_1, ψ_2 satisfy $\bar{\psi}_1 \bar{\psi}_2 = \chi_0$. The number of terms in $\sum_{\psi_1, \psi_2}$ is $(\delta - 1)^2$.

The number of terms in $\Sigma''_{\psi_1, \psi_2}$ is $\delta - 1$ and hence in Σ'_{ψ_1, ψ_2} there are $(\delta - 1)(\delta - 2)$ terms. Now we have

$$|\tau_{\psi_1} \tau_{\psi_2}| = p$$

[6] *Ibid.*, Satz 317.

The inner sum is, since every time $\bar{\psi}_1(r)\ \bar{\psi}_2(r)$ is a character $\chi(r)$ [and without loss of generality $0 < n < p$]

$$= \sum_{r=1}^{p-1} \epsilon^{-rn} \chi(r) = \sum_{r=1}^{p-1} \epsilon^{r(p-n)} \chi(r)$$

$$= \bar{\chi}(p-n) \sum_{r=1}^{p-1} \epsilon^{r(p-n)} \chi[r(p-n)] = \bar{\chi}(p-n) \sum_{r=1}^{p-1} \epsilon^{r} \chi(r) = \bar{\chi}(p-n)\, \tau_\chi.$$

Hence

$$|\Sigma| \leqslant |\Sigma'| + |\Sigma''| \leqslant (\delta-1)(\delta-2)\, p\sqrt{p} + (\delta-1).\ p.\ 1$$

whence

$$|A(p)| \leqslant \frac{(\delta-1)(\delta-2)}{\sqrt{p}} + \frac{\delta-1}{p}.$$

From this, as before, Theorem 2 follows.

5. Proof of Theorems 3 and 4.

Write,

$$S_\rho' = \sum_{h=1}^{q} \rho^{ah^{k_1}}$$

$$S_\rho'' = \sum_{h=1}^{q} \rho^{bh^{k_2}}$$

$$A(q) = q^{-2} \sum_{\rho} (S_\rho'\ S_\rho''\ \rho^{-n})$$

$M(p^l, n)$ is the number of solutions of

$$ah_1^{k_1} + bh_2^{k_2} \equiv n\ (p^l), \quad \text{with } 0 \leqslant h_1 < p^l, \quad 0 \leqslant h_2 < p^l.$$

It is easy to prove that (following *LV*, sätze 286 and 317)

$$1 + A(p) + \cdots + A(p^l) = p^{-l} M(p^l, n)$$

$$|A(p)| \leqslant \frac{1}{\sqrt{p}} (\delta_1 - 1)(\delta_2 - 1)$$

where $\delta_1 = (k_1, p-1)$ and $\delta_2 = (k_2, p-1)$.

The method of the proof is similar to that of Theorems 1 and 2. We need the following additional lemma, which takes the place of lemma 2.

Lemma 4. *If* $p \nmid 2k_1 k_2 n$, *then*

$$A(p^l) = 0 \qquad \text{for } l > 1.$$

Proof. We have

$$A(p^l) = p^{-2l} \sum_{\rho} (S_\rho'\ S_\rho''\ \rho^{-n}) = p^{-2l} \sum_{\rho} \Big(\sum_{h=1}^{p^l} \rho^{ah^{k_1}}\Big)\ S_\rho''\ \rho^{-n}$$

$$= p^{-2l} \sum_{\rho} \Big(\sum_{h}' \rho^{ah^{k_1}} + \sum_{h}'' \rho^{ah^{k_1}}\Big)\ S_\rho''\ \rho^{-n}$$

[where $\sum_h'$ denotes that h runs over a reduced residue system (mod p^l) and $\sum_h''$

denotes that h takes the remaining values less than and equal to p^l.] It is known (LV, satz 306) that for $q = p^l$, $p \nmid k_1$, $l > 1$ $\sum_h' \rho^{hk_1} = 0$ and therefore $\sum_h' \rho^{ah^{k_1}} = 0$ since $(a, p) = 1$.

Hence

$$A(p^l) = p^{-2l} \sum_\rho \left(\sum_h'' \rho^{ah^{k_1} - n}\right) S_\rho''$$

Now

$$p^{l-1} \nmid (ah^{k_1} - n) \text{ since } p|h,\ p \nmid n, \text{ and } l > 1.$$

It therefore follows (LV, satz 220) that [note $p \nmid (ah_1^k - n)$]

$$\sum_\rho \sum_h'' \rho^{ah^{k_1} - n} = 0$$

and hence when $l > 1$,

$$A(p^l) = 0.$$

This proves Theorem 4, of which Theorem 3 is an easy consequence.

VARIATION IN THE NOCTURNAL RADIATION FROM THE SKY WITH ZENITH DISTANCE AND WITH TIME DURING THE NIGHT.

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and
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(From the Meteorological Office, Poona.)

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1. Introduction.

Measurements of the heat radiation received by unit area of a horizontal surface from the whole sky during clear nights at Poona, have been discussed by Ramanathan and Desai[1] and by Raman[2]. Ramanathan and Ramdas[3] showed that the expression $\frac{S}{\sigma T^4} = A - B \times 10^{-\gamma e}$ (where S is the radiation coming from the sky, T is the temperature of the air near the measuring instrument, σ is the Stefan-Boltzman constant, A, B and γ are other constants and e is the pressure of water vapour near the place of observation) obtained empirically by Angstrom can be derived from a consideration of the variation of the absorption coefficient of water vapour in different parts of the spectrum in the region of long waves. Hourly observations of the heat radiation coming from the night sky during selected clear nights at Poona have been discussed recently by Raman.[4] These observations show that the heat radiation from the water vapour in the atmosphere decreases with time during the night, the maximum value being obtained immediately after sunset and the minimum value just before sunrise. In the same paper, Raman has also discussed simultaneous hourly observations of the radiation from the night sky recorded at different levels at and near Poona and shown that the magnitude of the nocturnal variation of the sky radiation is maximum near the ground and decreases rapidly with height. These results find an explanation in the fact that the S_3 radiation which comes from the air layers nearest to the measuring instrument should depend upon the temperature of these layers [*vide* paper (3) above]. The nocturnal variation of the air temperature in these layers is maximum near the ground level and the magnitude of ΔS_3, the variation of the S_3 radiation, is found to be of the same order as that of the variation of the total radiation S for all the wave-

lengths taken together. The importance of the lower regions of the atmosphere in controlling the radiative phenomena which we are discussing, is brought out clearly by these results.

Further consideration of the whole problem indicated that it would be worth-while to study the variation of the nocturnal radiation with zenith distance* and with time during the night. Hourly measurements of the radiation from different regions of the sky and its variation during the course of the night were made during a few nights towards the end of the last clear season (April—May, 1936). It is felt that a brief account of the experimental method and the conclusions which could be drawn from these preliminary observations would prove to be of interest.

2. *Description of Apparatus.*

The nocturnal radiation is measured with the help of a Moll's Micro-thermopile and a Moll's Micro-galvanometer, both of which possess the high degree of sensitiveness and quickness of response required for detecting the variation in the intensity of the radiation from different parts of the sky. The thermopile is mounted inside a box and packed with cello-tex boards on all sides. The box is provided with a small aperture (which subtends an angle of about 10° at the surface of the thermopile) through which radiation passes into the receiver of the thermopile. The aperture can be closed by means of two shutters, one of which works inside at the box temperatures while the other works outside the box. The shutter inside the box is usually opened after and closed before the one outside while making the measurements. Fig. 1 shows a sketch of the thermopile box, with the two shutters and the aperture. T is a thermometer passing through a hole at the top of the box with its bulb in contact with the metal casing of the thermopile. The thermometer registers the temperature of the instrument and may be read from outside.

The thermopile so mounted was calibrated by exposing the sensitive element to the hemispherical radiation from a hollow radiator coated with carbon deposited from camphor smoke (see Fig. 2) and noting the deflections of the galvanometer when the surface of the radiator was maintained steadily at different temperatures.

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* The variation of atmospheric radiation with zenith distance has been discussed by Angstrom (*Astrophysical Journal*, 1914, **39**, 1) and by W. H. Dines and L. H. G. Dines (*Mem. Roy. Met. Soc.*, 1927, **2**) by using experimental methods different from the method used in the present investigation.

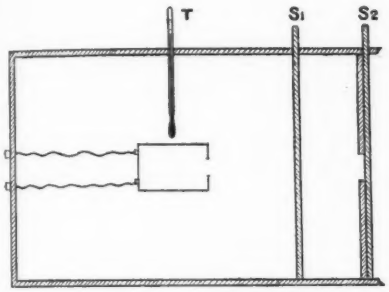

FIG. 1.
Thermopile.

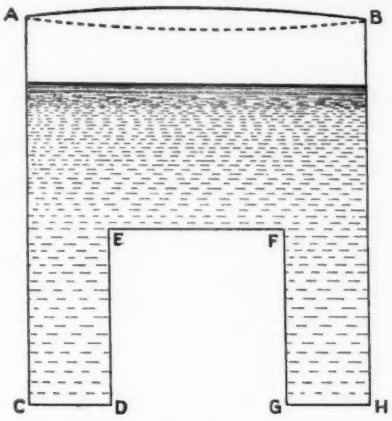

FIG. 2.
Radiator.

The thermopile was, after obtaining the calibration curve, taken outside into the open plot of the Central Agricultural Meteorological Observatory, for exposure to the different portions of the sky. When the aperture of the thermopile was facing upwards towards the zenith sky the deflection in the galvanometer was found to be steady and uninfluenced by any wind that might be playing round the instrument. For taking observations of the radiation from other angles, the instrument was tilted at the required angles in an azimuth opposite to that from which the wind, if any, was blowing. This precaution was found to be necessary and sufficient to obtain steady deflections in the galvanometer. The radiation from the sky at altitudes of 90° (vertical), 60°, 45°, 30°, 15° and 0° (horizontal) were recorded in the later experiments. Observations of the temperature of the air near the instrument and the pressure of water vapour in it were made with the help of an Assmann Psychrometer and the temperature of the thermopile was also read off each time the radiation observations were recorded. Observations of the total radiation coming from the whole sky were also recorded simultaneously with Angstrom's Pyrgeometer.

3. *Description of the Data.*

Attempts were made to record the hourly observations on a number of nights which were clear to start with. As the season was well advanced, however, on most of the nights alto-stratus or strato-cumulus clouds developed towards the morning. The preliminary observations recorded on the

25th April from the zenith sky and the fuller set of data recorded at different altitudes on the 2nd May 1936 were obtained from perfectly clear skies and the vapour pressure near the surface was also fairly steady. On the 30th April, however, there were traces of clouds at intervals; there was also a large change of vapour pressure at the surface but this did not alter the general trend of the results materially.

The data obtained on these three dates are discussed in the following pages.

TABLE I.

Measurements of Radiation from the zenith sky and other relevant meteorological observations taken during the night of the 25th April 1936.

Time in hours I. S. T.	Instrument Temperature °C.	Air Temperature near instrument °C.	Vapour pressure mm. of Hg.	Difference between temperature of 32°·8 C. and equivalent black body temperature of portion of sky concerned (△T)	Equivalent black body temperature T of portion of sky concerned °A.
1925	32·8	30·2	11·8	21·7	284·1
2010	30·8	28·7	12·1	21·8	284·0
2030	29·7	28·4	12·2	22·2	283·6
2100	28·8	27·8	12·7	22·5	283·3
2200	27·2	26·7	9·1	23·4	282·4
2300	25·5	25·7	13·1	24·4	281·4
2400	24·4	25·4	11·6	25·6	280·2
0100	23·1	23·8	13·3	27·2	278·6
0200	22·1	24·0	9·5	27·3	278·5
0300	21·5	23·0	9·3	28·0	277·8
0400	20·4	21·6	9·6	28·7	277·1
0500	19·5	21·4	7·7	29·0	276·8
0530	19·1	20·7	9·5	29·3	276·5

25th April 1936.—Table I gives the radiation observations recorded from the zenith sky on this date along with the other relevant data. Columns 1 to 4 of the table are self-explanatory. The deflections of the

galvanometer were corrected for the change of temperature of the thermopile from its initial value of 32°·8 C., using these corrected deflections the temperatures of a black body which, by exchange of radiation with the thermopile at 32°·8 C., would have caused these deflections were obtained from the calibration curve. We may call these black body temperatures the " equivalent black body temperatures " of the night sky. The differences between these temperatures from 32°·8 C. (ΔT) are given in column 5, while the equivalent black body temperatures themselves are given in the last column of the table. Fig. 3 shows the variation with time of the equivalent black body temperature of the zenith sky on this night. It will be seen that this temperature falls progressively as the night advances.

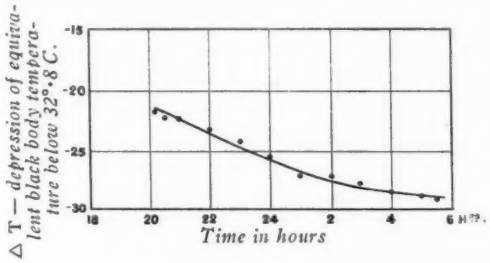

FIG. 3.

Nocturnal variation of the equivalent black body temperature of the zenith sky on 25-4-36.

30th April 1936.—On this day, the experiment was amplified so as to obtain simultaneous values of the equivalent black body temperatures of the sky at different vertical angles. A complete set of observations, at any hour, consisted in exposing the thermopile to the sky at the various vertical angles one after another. On the 30th April, the angles used were 90° (vertical), 60°, 45°, 30° and 15°. Table II gives the observations and the calculated data. The data presented in respect of each angle and the method of calculation are similar to those given in respect of the zenith sky for the 25th April in Table I. The values of ΔT in Table II are given as deviations from 34°.7 C., the initial temperature of the thermopile.

The curves in Fig. 4 (*a*) show the variation with time of the equivalent black body temperatures of the different altitudes of the sky mentioned against each curve. It will be observed that at each altitude the equivalent black body temperature shows a progressive fall with the advance of night, the fall becoming less rapid after midnight. The general characteristics of the variation at different altitudes are the same.

TABLE II.

Measurements of Radiation from the night sky from different altitudes and other relevant meteorological observations taken on the night of the 30th April 1936.

Time in hours I.S.T.	Instrument Temperature °C.	Air Temperature °C.	Vapour Pressure mm. of Hg.	Altitude – 90° (vertical)		Altitude—60°		Altitude—45°		Altitude—30°		Altitude—15°		Total radiation S from whole sky measured with Angstrom's pyrgeometer gm. cals./cm.²/min.
				△ T below 34°·7 C.	T (°A)	△ T below 34°·7 C.	T (°A)	△ T below 34°·7 C.	T (°A)	△ T below 34°·7 C.	T (°A)	△ T below 34°·7 C.	T (°A)	
(1)	(2)	(3	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
1935	34·7	33·8	16·7	18·5	289·2									0·566
2000	34·3	33·2	16·0	19·0	288·7	17·0	290·7	15·5	292·2	13·0	294·7			0·5[illegible]3
2030	33·2	32·5	15·3	19·7	288·0	18·0	289·7	17·2	290·5	13·7	294·0	8·5	299·2	0·564
2100	32·6	32·0	14·7	20·4	287·3	19·0	288·7	17·6	290·1	15·0	292·7	9·1	298·6	0·553
2200	31·4	30·9	14·5	20·0	286·7	19·7	288·0	19·0	288·7	16·2	291·5	11·0	296·7	0·542
2300	29·5	29·1	12·5	23·5	284·2	22·5	285·2	20·5	287·2	17·6	290·1	13·2	294·5	0·524
2400	27·7	27·3	10·7	24·7	283·0	23·7	284·0	22·5	285·2	20·1	287·6	15·0	292·7	0·512
0100	25·4	25·2	9·6	26·0	281·7	24·5	283·2	23·2	284·5	20·3	287·4	15·7	292·0	0·501
0200	24·2	24·4	9·0	25·2	282·5	24·5	283·2	23·0	284·7	20·5	287·2	15·5	292·2	0·496
0300	22·7	23·2	8·7	27·0	280·7	26·0	281·7	24·5	283·2	22·0	285·7	17·0	290·7	0·503
0400	21·6	23·8	10·1	26·2	281·5	25·7	282·0	24·5	283·2	21·5	286·2	16·1	291·6	0·500
0500	22·0	23·8	8·1	26·7	281·0	24·5	283·2	24·5	283·2	21·5	286·2	17·5	290·2	0·503

Range of variation °C.

△ T—*depression of equivalent black body temperature below* 34°·7 C.

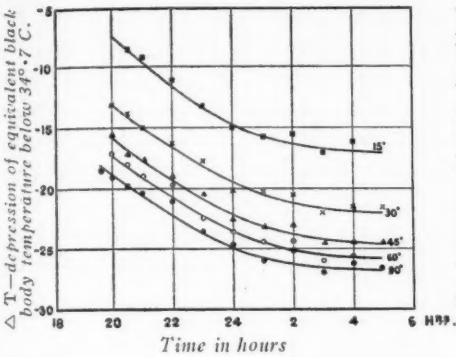

FIG. 4 (*a*).

Nocturnal variation of equivalent black body temperature at different altitudes of the sky on **30-4-1936.**

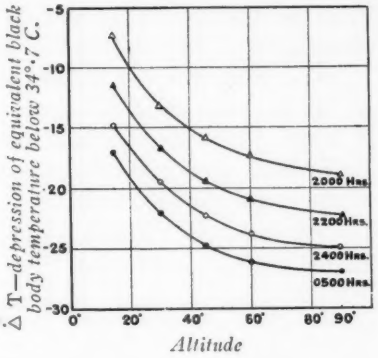

FIG. 4 (*b*).

Variation of equivalent black body temperature of the night sky with altitude at different hours on **30-4-1936.**

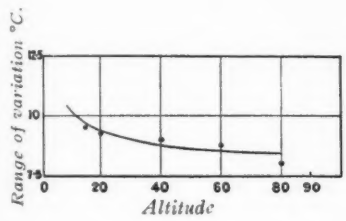

FIG. 4 (*c*).

Range of variation of equivalent black body temperature at different altitudes during the night of **30-4-1936.**

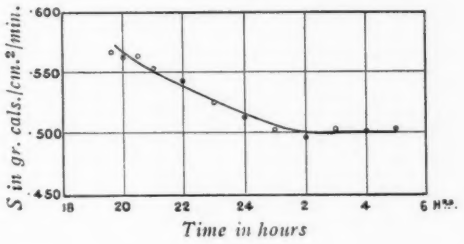

FIG. 4 (*d*).

Nocturnal variation of radiation S from whole sky as obtained from Pyrgeometer on **30-4-1936.**

The information is also presented in a slightly different form in Fig. 4 (*b*) where the simultaneous values of the equivalent black body temperatures at the different altitudes of the sky (*viz.*, 90°, 60°, 45°, 30° and 15°) as obtained from the smooth curves of Fig. 4 (*a*) are plotted ; the hour to which each curve of Fig. 4 (*b*) refers is noted against it. These curves show that at any particular instant the equivalent black body temperature of the sky decreases as the vertical angle increases. From Fig. 4 (*b*) the values of the range of variation through the night of the equivalent black body temperatures at different altitudes of the night sky can be estimated. These values are plotted in Fig. 4 (*c*) against the vertical angle. It will be seen that the variation is minimum near the zenith and increases as one approaches the horizontal direction. In the last column of Table II, the values of S the total radiation

from the sky measured with Angstrom's Pyrgeometer are also given for comparison. These values are also shown diagrammatically in Fig. 4 (*d*).

2nd May 1936.—A further improvement of the experiment was made on this day inasmuch as observations were taken at all the altitudes from 0° to 90°. The observations of this date were obtained under ideal conditions as the skies were perfectly clear throughout the night. They are the best of the series obtained so far.

The data are given in detail in Table III and are also represented by means of the curves in Figs. 5 (*a*), (*b*) and (*c*) which fully confirm the results

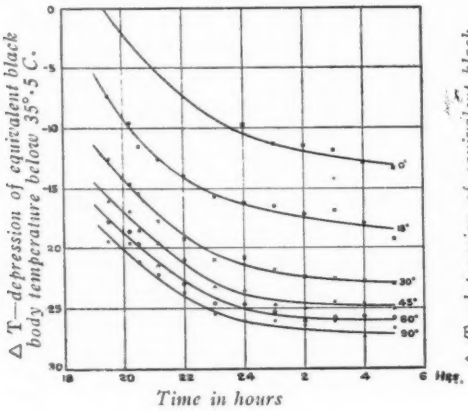

FIG. 5 (*a*).

Nocturnal variation of equivalent black body temperature at different altitudes of the sky on 2-5-1936.

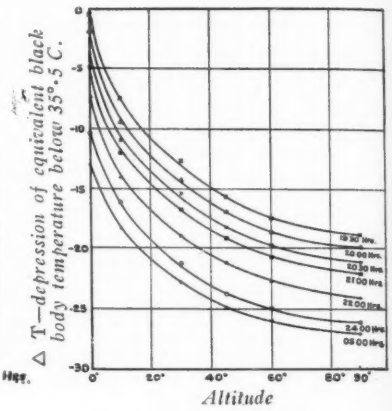

FIG. 5 (*b*).

Variation of equivalent black body temperature of the night sky with altitude at different hours on 2-5-1936.

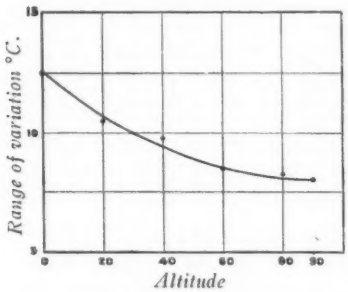

FIG. 5 (*c*).

Range of variation of equivalent black body temperature at different altitudes during the night of 2-5-1936.

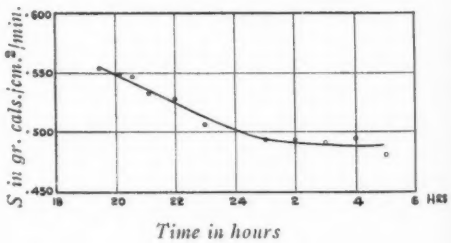

FIG. 5 (*d*).

Nocturnal variation of radiation S from whole sky as obtainad from Pyrgeometer on 2-5-1936.

TABLE III.

Measurements of Radiation from the night sky from different altitudes and other relevant meteorological observations taken on the night of the 2nd May 1936.

Time in hours I.S.T.	Instrument Temperature °C.	Air Temperature °C.	Vapour Pressure mm. of Hg.	Altitude 90° (vertical)		Altitude—60°		Altitude—45°		Altitude—30°		Altitude—15°		Altitude—0°		Total radiation S from whole sky measured with Angstrom's Pyrgeometer gm. cals./cm.²/min.
				Δ T below 35°·5 C.	T (°A)	Δ T below 35°·5 C.	T (°A)	Δ T. below 35°·5 C.	T (°A)	Δ T below 35°·5 C.	T (°A)	Δ T below 35°·5 C.	T (°A)	Δ T below 35°·5 C.	T (°A)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
1930	35·5	32·3	15·7	19·5	289·0	17·8	290·7	16·0	292·5	12·6	295·9	7·3	301·2			0·554
2010	33·0	30·8	16·5	19·6	288·9	18·6	288·9	16·9	291·6	14·7	293·8	9·6	298·9			0·549
2035	31·8	30·2	16·8	21·3	287·2	19·7	288·8	18·6	289·9	15·5	293·0	11·5	297·0			0·547
2110	30·4	29·0	15·3	22·2	286·3	21·5	287·0	19·7	288·8	17·8	290·7	12·6	295·9			0·532
2200	29·4	28·4	14·3	23·7	284·8	23·0	285·5	21·0	287·5	19·3	289·2	14·0	294·5			0·527
2300	27·8	28·0	12·0	25·5	283·0	24·6	283·9	23·2	285·3	21·0	287·5	15·7	292·8			0·506
2400	27·2	24·2	11·8	26·0	282·5	24·7	283·8	23·5	285·0	20·8	287·7	16·2	292·3	9·8	298·7	..
0100	25·6	25·8	12·8	26·0	282·5	25·3	283·2	24·8	283·7	21·8	286·7	16·5	292·0	11·2	297·3	0·494
0200	25·0	25·2	13·7	26·4	282·1	26·0	282·5	25·0	283·5	22·4	286·1	17·1	291·4	11·4	297·1	0·493
0300	24·6	24·8	14·2	26·0	282·5	25·8	282·7	24·5	284·0	22·5	286·0	16·9	291·6	11·7	296·8	0·490
0400	24·1	24·6	12·9	27·4	281·1	25·7	282·8	24·5	284·0	22·6	285·9	17·9	290·6	12·8	296·5	0·494
0500	23·2	23·0	11·4	26·6	281·9	25·8	282·7	25·0	283·5	23·0	285·5	19·3	289·2	13·4	295·1	0·480

of the 30th April. The values of ΔT in Table III are given as deviations from 35°·5 C., the initial temperature of the thermopile.

The intensity of the total radiation S from the night sky as measured with an Angstrom's Pyrgeometer at different hours on the night of the 2nd May 1936 are given in the last column of Table III, and shown diagrammatically in Fig. 5 (*d*).

From the data discussed above, two main conclusions emerge, *viz.*,

(i) there is a decrease with progress of night in the intensity of radiation coming from the different zones of the night sky, and

(ii) the decrease is maximum in the radiation coming from the horizontal direction and minimum from the zenith sky.

The first result is in agreement with the results discussed in the earlier paper (*vide* paper 4, *loc. cit.*) where it has been shown that there is a decrease with time in the nocturnal radiation from the night sky as a whole.

Regarding the second result, we should remember that the water vapour content of the atmosphere decreases rapidly with height and that the layers of equal water vapour content are horizontal. So far as the S_3 radiation is concerned, the radiation from a horizontal or vertical direction will be coming from the air layers in the immediate neighbourhood of the instrument; also, the variation of S_3 with time will be greater in a horizontal direction than in a vertical direction, because, the nocturnal cooling decreases with height. When we come to the S_2 radiation, however, we see that this radiation from a vertical direction will be coming from a region of the upper atmosphere which undergoes little or no cooling during the night. The S_2 radiation from a horizontal direction comes from air layers which are relatively nearer the instrument. As these layers experience the largest fall of temperature during the night, it follows that the S_2 radiation will also undergo a decrease with time during the night. The result is that in the horizontal direction both S_2 and S_3 vary whereas, in the vertical direction, S_2 does not undergo any change. We shall consider these details more fully in a later paper. The mean equivalent black body temperature of the night sky, as a whole, can be calculated in a simple manner from the zonal distribution of temperature and the results compared with the measurements of S with Angstrom's Pyrgeometer. This will be taken up after collecting more observational data during the coming winter.

Summary.

The hourly variation of the heat radiation coming from different altitudes of the night sky was measured on three nights in April and May 1936 with a Moll's Micro-galvanometer and a Micro-thermopile provided with a

small aperture. These observations show that the nocturnal cooling of the radiating air layers as shown by the decrease in the equivalent black body temperature of the sky is maximum for altitude zero (*i.e.*, horizontal) and minimum for altitude 90° (*i.e.*, zenith).

The authors have great pleasure in thanking the Director-General of Observatories for providing necessary facilities for the investigation.

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2. Raman, P. K., *Proc. Ind. Acad. Sci.*, 1935, **1**, 815.
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4. Raman, P. K., *Proc. Ind. Acad. Sci.*, 1936, **4**, 243.

ON THE FINE STRUCTURE OF THE BALMER LINES.

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1. Introduction.

SOME recent experiments[1] on the fine structure of the Balmer lines of Hydrogen have shown a disagreement between calculated and observed term values. Other experiments[2] reach the opposite conclusion that no such disagreement exists. Houston and Hsieh state that the order of the magnitude of the effect observed by them is α times the fine-structure separation (α = fine-structure constant), and that the theory of fine structure requires modification. They have further made the suggestion (pointed out by Bohr and Oppenheimer) that the discrepancy might perhaps be corrected by taking into account the interaction between the electron and the radiation field due to the transitions between several fine-structure levels.

Several attempts have been made to sharpen the theory of the fine structure so as to enable an explanation of this discrepancy. Heller and Motz[3] have attempted to replace the Coulomb potential of the nuclear field by the potential of a static field given by the new field theory of Born and Infeld.[4] Treating the difference between the Born and Coulomb potentials as a perturbation, they calculate the term shifts in the one electron Schrödinger problem and conclude that the corrections obtained, although in the right direction, are much too small to explain the observed discrepancy. They further state that a rigorous treatment with the Dirac eigenfunctions does not materially alter the situation. Another attempt using the Born potential has been made by Meixner.[5] In place of the Schrödinger wave equation employed by Heller and Motz, he uses the Pauli equation which takes account of spin and also the relativistic correction. Treating $\phi_B - \phi_C$ as a

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[1] W. V. Houston and Y. M. Hsieh, *Phys. Rev.*, 1934, **45**, 263.
R. C. Williams and R. C. Gibbs, *ibid.*, p. 475.

[2] F. H. Spedding, C. D. Shane and N. S. Grace, *Phys. Rev.*, 1935, **47**, 38.

[3] G. Heller and L. Motz, *Phys. Rev.*, 1934, **46**, 202.

[4] M. Born and L. Infeld, *Proc. Roy. Soc.*, 1934, **A144**, 425.

[5] J. Meixner, *Ann. der Phys.*, 1935, [5] **23**, 371.

perturbation the result is obtained that the spin and relativity corrections are half as large as those obtained from Schrödinger's theory. Nevertheless, the total correction is shown to be negligible if one uses for the electron the radius of Born's field theory. If, instead of this radius, the radius as modified by Born and Schrödinger[6] be used the result, as shown by Meixner, is that nearly 30% of the discrepancy can be explained.

I have attempted in this paper to estimate the order of magnitude of the corrections obtained by taking into account the interaction of the electron with its own radiation field. For this purpose, I have used Born's field theory since by its unitary nature this theory can be expected to take care of this interaction automatically. This has been made possible by the two recent papers of Born[7] on the unitary theory of field and matter wherein the effect of an external field is taken into consideration provided that the external field be subject to the restriction that it be constant over the "diameter" of the electron. If we observe that the radius of the electron is of the order of 10^{-13} cm. and the radius of the H-atom 10^{-8} cm., it is evident that the external field of the nucleus satisfies the restriction stated above.

The method of procedure I adopt is to calculate the energy of the electromagnetic field wherein the electron is a singularity and is acted upon by the "constant" nuclear field, following the steps indicated in the above two papers of Born. The energy is obtained as the sum of two terms W_0 and ΔW, the former being the energy unperturbed by the external field and ΔW the perturbation energy. I next employ this perturbation term in the wave equation and estimate the correction in the several spectral terms.

The result I have obtained is that, if we use the Born radius of the electron, the corrections due to the interaction of the electron and the radiation field are negligible.[8] If, on the other hand, we use the Born-Schrödinger radius the corrections obtained explain one or two per cent. of the discrepancy. The notion of the Born-Schrödinger radius is subject, however, to great theoretical difficulties. For one thing it would spoil the

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[6] M. Born and E. Schrödinger, *Nature*, 1935, **135**, 342.

[7] M. Born, *Proc. Ind. Acad. Sci.*, 1936, **3**, No. 1, 8; and *ibid.*, **3**, 2, 85.

[8] In a recent paper, Meixner (*Ann. der Phys.*, 1936, [5] **27**, 389) has treated the question of this correction by using the methods of Weisskopf and Wigner in Dirac's theory of radiation and has come to the same conclusion as mine. It is quite natural that this purely quantum treatment does not involve any question of radius of the electron. This paper deals comprehensively with the several possible theoretical aspects of the question.

beautiful coincidences in the phenomenon of scattering of light by light[9] on Born's classical field theory and Dirac's purely quantum hole theory. It would also contradict the value[10] $\pi e^4/mc^4$ (experimentally confirmed) of the cross-section for the scattering by electrons of light of long wave-length. If we, therefore, lay aside the Born-Schrödinger radius as untenable, we can conclude that the interaction of the electron and radiation field does not materially effect the energy levels. It is remarkable that this investigation and Meixner's totally different method should lead to identical conclusions.

2. Energy of Electron in Constant External Field.

We assume the field of the nucleus constant over the diameter of the electron and determine the energy of the latter following the method of Born in the two papers mentioned above. (See reference [7].)

The total field is written

$$\left.\begin{aligned} \vec{E} &= \vec{E}^e + \vec{E}^i\,; \quad \vec{B} = \vec{B}^e + \vec{B}^i \\ \text{and} \quad \vec{D} &= \vec{D}^e + \vec{D}^i\,; \quad \vec{H} = \vec{H}^e + \vec{H}^i \end{aligned}\right\} \tag{1}$$

where the e- and i-fields denote the external field and field due to the electron itself. At infinity the fields $\vec{E}^i$, $\vec{B}^i$, $\vec{D}^i$ and $\vec{H}^i$ all tend to zero. The energy is calculated from

$$W = \int U\, dv \tag{2}$$

where U is the energy-density given by

$$U = \sqrt{1 + \vec{D}^2 + \vec{B}^2 + \vec{S}^2} - 1 \tag{3}$$

and $$\vec{S} = (\vec{D} \times \vec{B}) = (\vec{E} \times \vec{H}).$$

We treat the e-fields as constants and also omit terms like $\vec{D}^{e2}$ within the square root expression. This last is permissible since we can confine ourselves, so far as the range of integration is concerned, to a small neighbourhood of the singularity wherein almost all the energy is concentrated and wherein the e-fields are negligible compared to the i-fields. In the purely electrical case

$$U = \frac{b^2}{4\pi}\sqrt{1 + \frac{\vec{D}^2}{b^2}} - 1 \tag{4}$$

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[9] See for *e.g.*, L. Euler, *Ann. der Phys.*, 1936, **26**, 398. Also M. Born, *Proc. Ind. Acad. Sci.*, 1935, **2**, No. 6, 533.

[10] See M. Born, *Naturw.*, 1932, **20**, 269; also, *Nature*, 1935, **136**, 952.

introducing the absolute field b and the conventional units. We assume the field $\vec{D}^e$ constant both in magnitude and direction and take the latter as the x-direction with the origin taken at the singularity. Thus we can take

$$\vec{D}^e \text{ as } (D^e = D_x{}^e,\ 0,\ 0)$$

and

$$\vec{D}^i \text{ as } \left(\frac{e}{r^2}\cdot\frac{x}{r},\ \frac{e}{r^2}\cdot\frac{y}{r},\ \frac{e}{r^2}\cdot\frac{z}{r}\right)$$

and put $\vec{D} = \vec{D}^e + \vec{D}^i$ in (4). This gives

$$W = \frac{b^2}{4\pi}\int_0^\infty\int_0^\pi \left(\sqrt{1 + \frac{D^{e2}}{b^2} + \frac{D^{i2}}{b^2} + \frac{2D^eD^i\cos\theta}{b^2}} - 1\right) 2\pi r^2 dr \sin\theta d\theta$$

θ being the angle between $\vec{D}^i$ and the x-direction.

$$\text{or, } W = \frac{b^2}{4\pi}\int_0^\infty\int_0^\pi \left(\sqrt{1 + \frac{D^{i2}}{b^2} + \frac{2D^eD^i\cos\theta}{b^2}} - 1\right) 2\pi r^2 dr \sin\theta d\theta$$

$$= \frac{b^2}{4\pi}\int\int \left(\sqrt{1 + \frac{D^{i2}}{b^2}}\left\{1 + \frac{2D^eD^i\cos\theta/b^2}{1 + D^{i2}/b^2}\right\}^{\frac{1}{2}} - 1\right) 2\pi r^2 dr \sin\theta d\theta.$$

Expanding the square root with the aid of the Binomial theorem up to the second power of D^e we find in virtue of

$$\int_0^\pi \cos\theta \sin\theta d\theta = 0, \qquad \text{that}$$

$$W = W_0 - \frac{b^2}{8\pi}\int_0^\infty\int_0^\pi \frac{D^{e2}D^{i2}\cos^2\theta/b^4}{(1 + D^{i2}/b^2)^{\frac{3}{2}}} 2\pi r^2 \sin\theta dr d\theta$$

$$= W_0 - \frac{D^{e2}}{6b^2}\int_0^\infty \frac{r^2 D^{i2}\, dr}{(1 + D^{i2}/b^2)^{\frac{3}{2}}}$$

$$= W_0 - \frac{D^{e2}r_0{}^4}{6}\int_0^\infty \frac{r^4 dr}{(r^4 + r_0{}^4)^{\frac{3}{2}}} \tag{5}$$

where

$$W_0 = \frac{b^2}{4\pi}\int\int \left(\sqrt{1 + \frac{D^{i2}}{b^2}} - 1\right) 2\pi r^2 dr \sin\theta d\theta$$

and we have made the substitutions $D^i = e/r^2$ and $b = e/r_0$, r_0 being the Born-radius[11] of the electron. The integral in (5) can be easily integrated

[11] See reference [4], p. 439.

by putting $r = r_0 x$ and is equal to

$$\frac{1}{r_0}\int_0^\infty \frac{x^4 dx}{(1+x^4)^{\frac{3}{2}}}$$

$$= -\frac{1}{2r_0}\int_0^\infty x\,\frac{d}{dx}\left(\frac{1}{\sqrt{1+x^4}}\right)dx$$

$$= \frac{1}{2r_0}\int_0^\infty \frac{dx}{\sqrt{1+x^4}} = \frac{f(0)}{2r_0}$$

where $f(0) - f(x) = \frac{1}{2}\,\mathrm{F}\left(\frac{1}{\sqrt{2}},\ 2 \text{ arc tan } x\right)$ and $\mathrm{F}\ (k,\ 2 \text{ are tan } x)$ is the Jacobian elliptic integral of the first kind for $k = \frac{1}{\sqrt{2}}$.

Hence (5) reduces to

$$\mathrm{W} = \mathrm{W}_0 - \frac{\mathrm{D}^{e^2}\, r_0^3}{12} f(0). \tag{6}$$

Expression (6) shows how, on the present theory, the energy is modified when the effect of the external field is taken into consideration. We now put in (6),

$$\mathrm{D}^e = \frac{Ze}{r^2} \tag{7}$$

the r being now referred to the nucleus as origin and obtain

$$\mathrm{W} = \mathrm{W}_0 - \frac{Z^2 e^2 r_0^3 f(0)}{12}\cdot\frac{1}{r^4} = \mathrm{W}_0 - \frac{\lambda}{r^4}. \tag{8}$$

We now proceed to use the second term on the right hand-side of (8) as a perturbation and obtain the modification in the fine structure.

3. *Theory of Fine Structure.*

The present position of the theory of fine structure is that the correct explanation is afforded by Dirac's theory of the electron which gives results in accord with Sommerfeld's formula derived on the basis of the old quantum theory. The approximate two-matrix method of Pauli also gives correct results and is equivalent to the original Schrödinger-Gordon-Klein wave equation with the proper correction for spin. We can write the complete wave equation where the relativistic variation of mass and the spin are taken into consideration in the form[12]

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(\mathrm{W}_0 + \frac{Ze^2}{r} - \mathrm{V}_{\text{rel.}} - \mathrm{V}_{\text{spin}}\right)\psi = 0 \tag{9}$$

where $\mathrm{V}_{\text{rel.}}$ and V_{spin} can be treated as perturbation terms and are of the form

[12] See for *e.g.*, O. Halpern u. H. Thirring, *Erg. Exakt. Naturw.*, **Bd. 8**, S. 423.

$$V_{rel.} \sim \frac{1}{r^2} \text{ and } V_{spin} \sim \frac{1}{r^3}. \tag{10}$$

A treatment of equation (9) by using perturbation methods amounts to finding the averages $\overline{1/r^2}$ and $\overline{1/r^3}$ with respect to the radial wave functions of the unperturbed Schrödinger wave equation and gives the same result as obtained by Pauli's equation[13]

$$\left\{W + e\phi + \frac{\hbar^2}{2m}\Delta + \frac{1}{2mc^2}(W + e\phi)^2 + \frac{ie\hbar}{4m^2c^2}(\vec{E}\vec{p}) - \frac{e\hbar}{4m^2c^2}(\sigma[\vec{E} \times \vec{p}])\right\} \psi = 0 \tag{11}$$

where W = total energy, σ = Pauli's spin matrix, Δ = diograd, $\vec{p} = \frac{\hbar}{i}$ grad.

We now take account of a further perturbation due to our equation (8), wherein the W_0 is really to be taken equal to the expression within brackets in the left-hand side of (9), and introduce it in (9). The modified wave equation can be written as

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(W_0 + \frac{Ze^2}{r} - V_{rel.} - V_{spin} - V_{field}\right)\psi = 0 \tag{12}$$

where $V_{field} \sim \frac{1}{r^4}$ is the perturbation term in (8) and can be taken to denote the interaction of electron and field.

Hence if ΔW be the energy correction we have

$$\Delta W = -\lambda\,\overline{1/r^4} \tag{13}$$

where the mean value is taken with respect to the radial Schrödinger function of the unperturbed equation.

Before proceeding to estimate the magnitude of the correction as shown by (13) it is necessary to remove a difficulty connected with $\overline{1/r^4}$ for the *s*-terms (*i.e.*, $l = 0$). A reference to Bethe's article p. 286 shows that this is equal to ∞, but we can get over the difficulty if we observe that for *s*-terms we are concerned with values of r nearly equal to zero and for such values we cannot neglect $e\phi = Ze^2/r$ as compared with the rest-energy $E_0 = mc^2$. This is the approximation made in deriving (11) from Dirac's exact wave equation. We have therefore to replace[14]

$$\frac{\overline{1}}{r^4} = \int R^2 \cdot \frac{1}{r^4} r^2 dr \text{ by } \int \frac{R^2 dr}{r^2(1 + e^2 z/mc^2 r)^2}$$

$$i.e., \text{ by } \int \frac{R^2 r^2 dr}{(r + \rho_0)^2} \qquad \text{where } \rho_0 = e^2/mc^2,\ z = 1 \tag{14}$$

and $R = R_{nl}$ is the radial Schrödinger function.

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[13] See Bethe, *Handb. d. Phys. z. Auf.*, **Bd.** 24/1, p. 305.

[14] See Bethe, *ibid.*, footnote on p. 307.

Further in integrating (14) we can take the limits as 0 and ρ_0 themselves and use for R_{nl} in this region the value[15]

$$R_{nl} \approx \frac{1}{(2l+1)!}\sqrt{\frac{(n+l)!}{(n-l-1)!\,2n}}\left(\frac{2z}{n}\right)^{\frac{3}{2}+l} r^l \tag{15}$$

An elementary calculation obtained by putting (15) in (14) and integrating between the limits 0 and ρ_0 shows that for s-terms no mistake would be committed as regards order of magnitude if $\overline{1/r^4}$ were to be put equal to unity multiplied by Z^4/a_H^4.

As regards higher terms like p- and d-terms the values of the numerical factors of $\overline{1/r^4}$ for $l = 1, 2$, etc., are small fractions which have all been calculated in Bethe's tables referred to above. Hence we can take the order of magnitude of the energy correction due to the interaction of the radiation and the electron as

$$\Delta W \sim \lambda Z^4/a_H^4 \sim Z^6 e^2 r_0^3 f(0)/12 a_H^4. \tag{16}$$

With $Z = 1$, the correction in the wave number is given by

$$\frac{\Delta \nu_H}{c} \sim \frac{e^2 r_0^3 f(0)}{12hc\, a_H^4} = \frac{a r_0^3 f(0)}{2\pi \times 12\, a_H^4} \text{ cm.}^{-1} \tag{17}$$

where a is the fine-structure constant given by $a = 7{\cdot}28 \times 10^{-3}$.
Putting in (17), $r_0 = 2{\cdot}28 \times 10^{-13}$

$$\text{and} \quad a_H = \frac{\hbar^2}{me^2} = 0{\cdot}532 \times 10^{-8} \text{ cm.}$$

$$f(0) = 1{\cdot}8,$$

we obtain

$$\frac{\Delta \nu_H}{c} \sim 4 \times 10^{-9} \text{ cm.}^{-1}$$

If we observe that the discrepancy actually observed is of the order 10^{-3} cm.$^{-1}$ it will be seen that the correction obtained is negligible.

If, however, the Born-Schrödinger radius be substituted in (17) we have, since this radius is nearly equal to 14 r_0,

$$\frac{\Delta \nu_H}{c} \sim 2 \times 10^{-5} \text{ cm.}^{-1}$$

i.e., only about two per cent. of the discrepancy is explained. We might therefore conclude that the corrections obtained are negligible.

4. Conclusion.

I wish to thank Prof. Max Born who suggested this problem to me in the winter of 1935 and also indicated the method of procedure to be adopted.

[15] Bethe, *ibid.*, p. 283.

A REMARKABLE PROPERTY OF THE INTEGERS MOD N, AND ITS BEARING ON GROUP-THEORY.

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I. The Classification of the Elements of a Group into Conjugate Sets.

LET $S_1, S_2, \ldots\ldots S_n$ be the elements of a group G of order n, and let S_1 be the identity-element E of the group. The elements which are permutable with an assigned element S_i form a subgroup H of G, of order $\frac{n}{d}$ say. The n elements of G fall into d equinumerous subclasses with respect to H, namely

$$H, HS_p, HS_q, \ldots \qquad (1)$$

By definition of H, whatever element S of H we take, we have

$$S^{-1} S_i S = S_i ;$$

and therefore also,

$$(SS_p)^{-1} S_i S S_p = S_p^{-1} S^{-1} S_i S S_p = S_p^{-1} S_i S_p.$$

Thus the value of the transform $T^{-1}S_iT$ depends solely on the subclass (1) to which T belongs, so that there are exactly d transforms of S_i (including S_i itself), S_i and its transforms constitute ' a complete set of conjugate elements ' of G. Thus the n elements of G fall into a number (say r) of complete conjugate sets $C_1, C_2, \ldots\ldots, C_r$; where C_i contains h_i elements, h_i being necessarily a divisor of n, and

$$h_1 + h_2 + \cdots + h_r = n.$$

The identity element E constitutes by itself a complete conjugate set, and we can take $C_1 = E$, $h_1 = 1$.

The fundamental property of this division is that *the classes C combine among themselves by the group-operation*. We mean by this that each element of C_k occurs the same number $\gamma_{ij}{}^k$ of times among the h_ih_j elements C_iC_j, obtained by multiplying each element of C_i by each element of C_j. To prove this we have only to observe that if an element c_k of C_k occurs exactly t times in the product-set C_iC_j, then $T^{-1}c_kT$ must also occur exactly t times in the set $T^{-1}C_iC_jT = T^{-1}C_iT.T^{-1}C_jT = C_iC_j$, and that by proper choice of T, $T^{-1}c_kT$ will coincide with any element of C_k. It follows that the classes C can be taken as the elements of a linear algebra with the multiplication scheme

$$C_iC_j = \sum_k \gamma_{ij}{}^k C_k.$$

This is the ' algebra of conjugate sets ' or the ' Frobenius algebra ' associated with G.

It is clear that there exist other divisions of the elements of G into classes which combine among themselves by the group-operation (in the sense explained). To begin with there is the trivial division into n classes, each class containing only a single element; there is also the equally trivial division in which there is only one class which contains all the elements. More generally it is easy to see that if G_1 is any subgroup of G, there is a class-division of this kind determined by G_1; namely, an element S of G and all the elements which arise by transforming S *by any element of* G_1 are put into a class C_i. The proof that the classes C_i thus arising combine among themselves by the group-operation, is word for word the same as before. For, if an element c_k of C_k occurs exactly t times in the product C_iC_j, then if g is any element of G_1, $g^{-1}c_kg$ should also occur exatly t times in the set $g^{-1}C_iC_jg = g^{-1}C_ig.g^{-1}C_j.g = C_iC_j$; and by definition of C_k, $g^{-1}c_kg$ can represent any element of C_k by suitable choice of g.

If $G_1 = E$, we have the trivial division into n classes, each containing a single element; if $G_1 = G$ we have the Frobenius division into classes of conjugate sets. It is also clear that the classes corresponding to a general subgroup G_1 arise by a subdivision of the conjugate sets. We note also that if G is an Abelian group, then each element of G is a complete conjugate set by itself, and therefore the only division of G by this method into classes which combine among themselves by the group-operation, is the trivial division in which each class consists of a single element.

We proceed now to study a class-division of the integers mod N, which apart from its intrinsic importance, will shew that the above class-division of a group is not the most general one in which the classes combine by the group-operation. The property to be proved, of this class-division of the integers mod N does not seem to have been noticed before in mathematical literature; this is surprising in view of its fundamental character, and its importance in Additive Number-Theory.

We return in V to the question of class-division of a group.

II. The Algebra of Classes Mod N.

Let $t_1 = 1, t_2, t_3, \ldots, t_m = N$ be the distinct divisors of the integer N. The N numbers 1, 2, ..., N, considered as the representatives of the N distinct residue classes mod N, may be divided into m classes, $C_1, C_2, \ldots, C_m$, where C_i consists of the numbers whose greatest common divisor with N is t_i. In particular, C_1 consists of the $\phi(N)$ numbers less than and prime to N; C_i

contains evidently $\phi\left(\frac{N}{t_i}\right)$ numbers, and the fact that these classes exhaust the N numbers is expressed by the well-known relation :

$$\Sigma\phi\left(\frac{N}{t_i}\right) = \Sigma\phi\ (t_i) = N.$$

It is clear that the classes C combine among themselves by multiplication ; for, if t_k be the *g.c.d.* (greatest common divisor) of N and t_it_j, the $\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)$ numbers obtained by myltiplying each number of C_i by each number of C_j are identical mod N with the $\phi\left(\frac{N}{t_k}\right)$ numbers of C_k each repeated the same number of times. This is not however the remarkable property referred to in the title of this paper ; the remarkable property is that *the classes* C *combine among themselves by addition.* The proof of this is on the same lines as in the case of the group. If c_k, a number of the class C_k, occurs exactly t times among the $\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)$ numbers $C_i + C_j$ mod N, then if h is any number prime to N, hc_k must also occur exactly t times in the set :

$$h\ (C_i + C_j) = hC_i + hC_j = C_i + C_j.$$

By suitable choice of h, hc_k can represent any number whatever of the class C_k. Thus every number of the class C_k occurs the same number $\gamma_{ij}{}^k$ of times among the numbers $C_i + C_j$ mod N.

To construct an algebra of the classes C analogous to the Frobenius algebra of a group, it will be convenient to change the notation, and let + denote logical addition (*i.e.*, addition of aggregates), and indicate by $C_i \times C_j = C_iC_j$ the set of numbers obtained by *adding* each number of C_i to each number of C_j. With this notation, our result takes the form :

$$C_iC_j = \sum_k \gamma_{ij}{}^k\, C_k,$$

where the $\gamma_{ij}{}^k$'s are positive integers or zero.

As an illustration, take $N = 36 = 2^23^2$. The divisors are :

$$t_1 = 1\ ;\ t_2 = 2\ ;\ t_3 = 3\ ;\ t_4 = 4\ ;\ t_5 = 6\ ;\ t_6 = 9\ ;\ t_7 = 12\ ;\ t_8 = 18\ ;\ t_9 = 36.$$

The classes are :

$C_1 = (1, 5, 7, 11, 13, 17, 19, 23, 25, 29, 31, 35).$
$C_2 = (2, 10, 14, 22, 26, 34).$
$C_3 = (3, 15, 21, 33).$
$C_4 = (4, 8, 16, 20, 28, 32).$
$C_5 = (6, 30).$

$C_6 = (9, 27).$
$C_7 = (12, 24).$
$C_8 = (18).$
$C_9 = (36).$

Since C_9 is the zero residue-class $C_iC_9 = C_i$. The multiplication scheme for the remaining eight classes is as follows:

$$C_1^2 = 6C_2 + 6C_4 + 12C_5 + 12C_7 + 12C_8 + 12C_9.$$
$$C_1C_2 = 3C_1 + 6C_3 + 6C_6.$$

$C_1C_3 = 4C_2 + 4C_4$
$C_1C_4 = 3C_1 + 6C_3 + 6C_6$
$C_1C_5 = 2C_1$
$C_1C_6 = 2C_2 + 2C_4$
$C_1C_7 = 2C_1$
$C_1C_8 = C_1$
$C_2^2 = 3C_4 + 6C_7 + 6C_9$
$C_2C_3 = 2C_1$
$C_2C_4 = 3C_2 + 6C_5 + 6C_8$
$C_2C_5 = 2C_4$
$C_2C_6 = C_1$
$C_2C_7 = 2C_2$

$C_2C_8 = C_4$
$C_3^2 = 2C_5 + 2C_7 + 4C_8 + 4C_9$
$C_3C_4 = 2C_1$
$C_3C_5 = C_3 + 2C_6$
$C_3C_6 = 2C_5 + 2C_7$
$C_3C_7 = C_3 + 2C_6$
$C_3C_8 = C_3$
$C_4^2 = 3C_4 + 6C_7 + 6C_9$
$C_4C_5 = 2C_2$
$C_4C_6 = C_1$
$C_4C_7 = 2C_4$
$C_4C_8 = C_4$

$C_5^2 = C_7 + 2C_9$
$C_5C_6 = C_3$
$C_5C_7 = C_5 + 2C_8$
$C_5C_8 = C_7$
$C_6^2 = 2C_8 + 2C_9$
$C_6C_7 = C_3$
$C_6C_8 = C_6$
$C_7^2 = C_7 + 2C_9$
$C_7C_8 = C_5$
$C_8^2 = C_9$

III. The Evaluation of $\gamma_{ij}{}^k$.

THEOREM I. *If* t *is a divisor of* N, *the* $\phi(N)$ *numbers prime to* N *fall into* $\phi(t)$ *sets, each set consisting of* $\frac{\phi(N)}{\phi(t)}$ *numbers equal to each other mod* t.

For, if M is prime to N (and therefore to t), the numbers

$$M + t,\ M + 2t,\ \cdots,\ M + \frac{N}{t}\cdot t,$$

are distinct mod N, and equal mod t. To find the number of these numbers which are prime to N, we note that none of these numbers are divisible by any prime factor of t. Let $p_1, p_2, \ldots\ldots$ be the prime factors of $\frac{N}{t}$ which do not occur in t. The condition,

$$M + rt \not\equiv 0 \bmod p_1, p_2, \ldots,$$

gives

$$r \not\equiv -\frac{M}{t} \bmod p_1, p_2, \cdots$$

Thus the required number is the number of residue classes-mod $\left(\frac{N}{t}\right)$, which are not equal to $-\frac{M}{t}$ mod p_1 or p_2 or..... By the familiar

argument which is used in evaluating Euler's function $\phi(N)$, this number is

$$\frac{N}{t}\left(1-\frac{1}{p_1}\right)\left(1-\frac{1}{p_2}\right)\cdots=\frac{\phi(N)}{\phi(t)}.$$

Thus the $\phi(N)$ numbers prime to N consist of sets of $\frac{\phi(N)}{\phi(t)}$ numbers equal to each other mod t. It is clear that there is one such set corresponding to each residue-class mod t, prime to t.

Cor. If M is a given number prime to N, there are $\frac{\phi(N)}{\phi(t)}$ numbers. M′ prime to N, such that $M+M'\equiv 0 \bmod t$. For M′ is one of the set of $\frac{\phi(N)}{\phi(t)}$ numbers equal to $-M \bmod t$.

THEOREM II. $\gamma_{11}^{k}=\phi(N)\cdot\Pi\left(1-\frac{1}{p-1}\right)$, *where the product extends over all the prime factors of N which do not occur in* t_k.

For, by Theorem I Cor. there occur among the $\{\phi(N)\}^2$ numbers of the set C_1^2, precisely $\frac{\{\phi(N)\}^2}{\phi(t_k)}$ which are divisible by t_k. In order that a number divisible by t_k may belong to the class C_k, it is necessary and sufficient that it be not divisible by $t_k\ p_i$ for any prime factor p_i of $\frac{N}{t_k}$. Hence the number of numbers of the set C_1^2 that belong to C_k is :

$$\{\phi(N)\}^2\left\{\frac{1}{\phi(t_k)}-\Sigma\frac{1}{\phi(t_kp_i)}+\Sigma\frac{1}{\phi(t_kp_ip_j)}-\Sigma\frac{1}{\phi(t_kp_ip_jp_k)}+\cdots\right\}$$

But by definition of γ_{11}^{k}, this number is $\gamma_{11}^{k}\,\phi\left(\frac{N}{t_k}\right)$. Hence

$$\gamma_{11}^{k}=\frac{\{\phi(N)\}^2}{\phi\left(\frac{N}{t_k}\right)}\cdot\left\{\frac{1}{\phi(t_k)}-\Sigma\frac{1}{\phi(t_kp_i)}+\cdots\right\}.$$

Now the prime factors of $\left(\frac{N}{t_k}\right)$ may be divided into two groups $(q_1, q_2\cdots)$ and $(p_1, p_2,\cdots)$, where the q's occur in t_k and the p's do not occur in t_k. It is clear that $\phi(t_kq_i)=q_i\,\phi(t_k)$ and $\phi(t_kp_i)=\phi(t_k)(p_i-1)$. Hence :

$$\gamma_{11}^{k}=\frac{\{\phi(N)\}^2}{\phi\left(\frac{N}{t_k}\right)\phi(t_k)}\cdot\Pi\left(1-\frac{1}{q_i}\right)\cdot\Pi\left(1-\frac{1}{p_i-1}\right).$$

Since $\phi\left(\frac{N}{t_k}\right)\phi(t_k)=\phi(N)\cdot\Pi\left(1-\frac{1}{q_i}\right)$, we have finally

$$\gamma_{11}^{k}=\phi(N)\cdot\Pi\left(1-\frac{1}{p_i-1}\right).$$

Cor. γ_{11}^{k} vanishes only when N is even and t_k odd. When N is odd, $\gamma_{11}^{k}\neq 0$, and therefore all classes are represented in C_1^2.

THEOREM III. *If* t_{ij} *be the* g.c.d. *of* t_i, t_j, *the* $\phi\left(\frac{N}{t_i}\right)$ *numbers of* C_i *fall into* $\phi\left(\frac{t_j}{t_{ij}}\right)$ *equinumerous sets of numbers equal to each other mod* t_j. *To each number of class* (t_{ij}) *mod* t_j, *there corresponds one of these sets.*

For if T_i be a number of C_i, the numbers

$$T_i + t_j, \quad T_i + 2t_j, \cdots, \quad T_i + \frac{N}{t_j} \cdot t_j,$$

are distinct mod N and equal mod t_j. We shall shew that exactly $\phi\left(\frac{N}{t_i}\right) \Big/ \phi\left(\frac{t_j}{t_{ij}}\right)$ of these numbers belong to C_i. The statements of the theorem follow then without difficulty.

Now if $T_i + rt_j$ is to be divisible by t_i, r must be divisible by $\frac{t_i}{t_{ij}}$. Hence the numbers of the above series which are divisible by t_i are :

$$T_i + \lambda \cdot \frac{t_i}{t_{ij}} \cdot t_j; \quad \lambda = 1, 2, \cdots, \frac{N\, t_{ij}}{t_i t_j}.$$

Out of these, the numbers that belong to C_i are those for which

$$\frac{T_i}{t_i} + \lambda \frac{t_j}{t_{ij}} \text{ is prime to } \frac{N}{t_i}.$$

By the reasoning of Theorem I, the number of values of λ for which this is the case is

$$\phi\left(\frac{N}{t_i}\right) \Big/ \phi\left(\frac{t_j}{t_{ij}}\right).$$

This proves the required result. Since this number is independent of the particular number T_i of C_i, there follows the division of C_i into equinumerous subclasses mod t_j, which are respectively equivalent to all the numbers mod t_j which have the g.c.d. t_{ij} with t_j.

Cor. (1) If T is a given number of C_i, the number of numbers T′ of C_i, for which $T + T' = 0 \pmod{t_j}$ is by this theorem, the number belonging to a particular subclass of C_i—namely,

$$\phi\left(\frac{N}{t_i}\right) \Big/ \phi\left(\frac{t_j}{t_{ij}}\right).$$

Cor. (2) If c_i represents an arbitrary number of C_i, the congruence

$$c_i + c_j = 0 \pmod{t_k},$$

has no solution, if the *g.c.d.* t_{ik} of t_i, t_k is not identical with t_{jk}. If $t = t_{ik} = t_{jk}$, the number of solutions of the congruence is :

$$\frac{\phi\left(\frac{N}{t_i}\right) \phi\left(\frac{N}{t_j}\right)}{\phi\left(\frac{t_k}{t}\right)}.$$

The first part is a direct consequence of the theorem. To prove the second part, we have only to observe that to solve the congruence, we may choose for c_i any number of C_i, and then c_j must belong to a particular subclass of C_j mod t_k.

THEOREM IV. *If c_λ represents an arbitrary number of C_λ, the equation*

$$c_i + c_j = c_k \pmod{N}$$

has no solution unless $t_{ij} = t_{ik} = t_{jk} = t$ (where t_{ij} is the g.c.d. *of t_i, t_j); if these conditions are satisfied the number of solutions is:*

$$\frac{\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)\phi\left(\frac{N}{t_k}\right)}{\phi\left(\frac{N}{t}\right)} \cdot \prod_q \left(1 - \frac{1}{q-1}\right)$$

where the product extends over all those prime factors q *of* $\frac{N}{t_k}$ *which do not occur in* $\frac{t_k}{t}, \frac{t_i}{t}, \frac{t_j}{t}$.

For, by Theorem III Cor. (2), the number of solutions $f(t_k)$ of $c_i + c_j = 0 \pmod{t_k}$ is $\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)\Big/\phi\left(\frac{t_k}{t}\right)$ if $t_{ik} = t_{jk} = t$ (say) and zero otherwise.

Hence if $t_{ik} = t_{jk} = t$, the number of cases in which $c_i + c_j$ belongs to C_k is:

$$f(t_k) - \Sigma f(t_k p_1) + \Sigma f(t_k p_1 p_2) - \ldots.$$

where the p's are all the prime factors of $\frac{N}{t_k}$.

Now $f(t_k p_1 p_2 \ldots.)$ is zero except when the two *g.c.d.*'s

$$(t_k p_1 p_2 \ldots., t_i), \quad (t_k p_1 p_2 \ldots., t_j) \tag{1}$$

are identical; that is, unless the two *g.c.d.*'s

$$\left(\frac{t_k}{t} p_1 p_2 \cdots, \frac{t_i}{t}\right), \quad \left(\frac{t_k}{t} p_1 p_2 \cdots, \frac{t_j}{t}\right)$$

are identical. Remembering that t_k/t is prime both to t_i/t and to t_j/t, it is necessary for the identity of these two *g.c.d.*'s that each of the primes $p_1, p_2 \ldots$ should occur either in both or in neither of $t_i/t, t_j/t$. But if there are common factors of $t_i/t, t_j/t$, it is easy to see that the series:

$$f(t_k) - \Sigma f(t_k p_1) + \Sigma f(t_k p_1 p_2) - \cdots$$

$$= \phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)\left\{\frac{1}{\phi\left(\frac{t_k}{t}\right)} - \Sigma \frac{1}{\phi\left\{\frac{t_k p_1}{(t_i, t_k p_1)}\right\}} + \Sigma \frac{1}{\phi\left\{\frac{t_k p_1 p_2}{(t_i, t_k p_1 p_2)}\right\}} \cdots\right\} \tag{2}$$

[where the p's are the prime factors which occur in both or in neither of t_i/t, t_j/t, and (a, b) denotes the g.c.d. of a and b] must be identically zero. Hence

the number of solutions required in the theorem is 0 unless $t_{ij} = t = t_{ik} = t_{jk}$ [this is indeed directly evident from the equation $c_i + c_j = c_k \pmod{N}$]. Assuming then this condition satisfied, the p's in the series (2) do not occur in t_i/t or t_j/t, so that

$$(t_i,\ t_k\ p_1p_2\ldots.) = t. \tag{3}$$

Now divide the p's in (2) into two classes according as they do or do not occur in t_k/t ; denote the p's of the former class by p and those of the latter class by q. We have then

$$\phi\left\{\frac{t_k,\ p_1p_2\cdots q_1q_2\cdots}{(t_i,\ t_kp_1p_2\cdots q_1q_2\cdots)}\right\} = \phi\left(\frac{t_k}{t}\cdot\ p_1p_2\cdots q_1q_2\cdots\right)\ [\text{(by 3)}]$$

$$= \phi\left(\frac{t_k}{t}\right)\cdot\ p_1p_2\cdots\ (q_1-1)\ (q_2-1)\cdots$$

Hence the series (2) reduces to :

$$\frac{\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)}{\phi\left(\frac{t_k}{t}\right)}\ \Pi\left(1-\frac{1}{p}\right)\cdot\ \Pi\left(1-\frac{1}{q-1}\right) \tag{4}$$

Now since the p's are common prime factors of N/t_k and t_k/t, we have

$$\phi\left(\frac{N}{t}\right)\cdot\ \Pi\left(1-\frac{1}{p}\right) = \phi\left(\frac{N}{t_k}\right)\phi\left(\frac{t_k}{t}\right)\cdot$$

Hence (4) reduces to :

$$\frac{\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)\phi\left(\frac{N}{t_k}\right)}{\phi\left(\frac{N}{t}\right)}\cdot\ \Pi\left(1-\frac{1}{q-1}\right),$$

which proves the theorem.

Cor. (1). Let $g_1 = t$ be the g.c.d. of t_i, t_j, t_k, g_2 the g.c.d. of their l.c.m.'s two at a time, and g_3 their l.c.m. The Theorem states that the number of solutions of $c_i + c_j = c_k \pmod{N}$ is zero, unless $g_2 = g_1 = t$. When this condition is satisfied the expression for the number of solutions given in the theorem, is equivalent to :

$$\phi\left(\frac{N}{g_3}\right)\phi\left(\frac{N}{t}\right)\cdot\ \Pi\left(1-\frac{1}{q-1}\right),$$

where the product extends over the prime factors q of N/t, which do not occur in g_3/t. To prove this, write

$$t_i = t\mathrm{T}_i,\ t_j = t\mathrm{T}_j,\ t_k = t\mathrm{T}_k\ ;\ g_3 = t\mathrm{T}_i\ \mathrm{T}_j\ \mathrm{T}_k,$$

where every two of T_i, T_j, T_k are relatively prime. It follows easily that

$$\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)\phi\left(\frac{N}{t_k}\right) = \phi\left(\frac{N}{g_3}\right)\left[\phi\left(\frac{N}{t}\right)\right]^2.$$

Further, the prime factors of $N/t_k = N/tT_k$ which do not occur in T_i, T_j, T_k are identical with the prime factors of N/t which do not occur in g_3/t.

Hence the alternative form.

Cor. (2). It is clear that the number of solutions required in the theorem is equal to $\gamma_{ij}{}^k\ \phi(N/t_k)$. Hence

$$\gamma_{ij}{}^k = \frac{\phi\left(\frac{N}{t_i}\right)\phi\left(\frac{N}{t_j}\right)}{\phi\left(\frac{N}{t}\right)} \cdot \Pi\left\{1 - \frac{1}{q-1}\right\} \text{ or } 0,$$

according as the g.c.d. of every two of t_i, t_j, t_k is the same number t or not, the product extending over the prime factors q of $\frac{N}{t}$ which do not occur in $\frac{t_i}{t}$, $\frac{t_j}{t}$ or $\frac{t_k}{t}$.

IV. Alternative Evaluation of $\gamma_{ij}{}^k$ by the Theory of Multiplicative Functions.

The above direct evaluation of $\gamma_{ij}{}^k$ will now be confirmed by a less direct but more elegant method. The number of solutions of

$$c_i + c_j = c_k \bmod N,$$

is equal to $\phi(N/t_k)\ \gamma_{ij}{}^k$. Now, m and $-m$ always belong to the same class mod N. Hence this number of solutions is also the number of solutions of

$$c_i + c_j + c_k = 0 \bmod N.$$

It is clear that this number $\nu(N, t_i, t_j, t_k)$ (say) is a symmetric function of t_i, t_j, t_k. More generally we may define the function $\nu(N, M_1, M_2, M_3)$ as the number of solutions of

$$c_1 + c_2 + c_3 = 0 \bmod N,$$

with the condition that c_i is to belong to the same class mod N as M_i ($i = 1, 2, 3$). It is clear that $\nu(N, M_1, M_2, M_3)$ is a function symmetric in the arguments (M_1, M_2, M_3) and depending on M_1, M_2, M_3 only through the residue classes mod N, to which they belong.

THEOREM V. *The function $\nu(N, M_1, M_2, M_3)$ is a multiplicative* function of its four arguments.*

For the Chinese remainder theorem asserts that if N,N′ be relatively prime, there is a unique number mod NN′ which is equal to two given numbers

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* A function $f(M_1, M_2, \ldots)$ of positive integral arguments is said to be *multiplicative* if $f(M_1N_1, M_2N_2 \ldots) = f(M_1, N_2, M_2N_2 \ldots)\ f(N_1, N_2, \ldots)$ whenever $(M_1M_2 \ldots)$ is prime to $(N_1N_2 \ldots)$. For the properties of such functions, see R. Vaidyanathaswamy, "*The Theory of Multiplicative Arithmetic Functions*," *Trans. Am. Math. Soc.*, 33, 2, pp. 579-662.

mod N and N′ respectively. Further the unique number mod NN′ which is equal to a number of class t (a divisor of N) mod N, and to a number of class t' mod N′ must evidently belong to class tt' mod NN′ ; and conversely. Now let t_i be the g.c.d. (N, M_i) and t_i' the g.c.d. (N′, M_i'). If $NM_1M_2M_3$ be prime to $N'M_1'M_2'M_3'$, then ν (NN′, M_1M_1', M_2M_2', M_3M_3') is the number of solutions of the equation :

$$k_1 + k_2 + k_3 = 0 \text{ mod } NN', \tag{1}$$

where k_i belongs to the class t_it_i' mod NN′. This implies each of the equations

$$k_1 + k_2 + k_3 = 0 \text{ mod } N \tag{2}$$

$$k_1 + k_2 + k_3 = 0 \text{ mod } N_1' \tag{3}$$

where k_i is a number of class t_i in (2) and a number of class t_i' in (3). Thus each solution of (1) yields a unique solution of (2) and a unique solution of (3). Conversely, since there is, by the Chinese remainder theorem, a unique number of class t_it_i' mod (NN′) which is equal mod N to a given number of class t_i, and mod N′ to a given number of class t_i', it follows that any solution of (2) can be combined with any solution of (3) so as to produce a unique solution of (1). Hence the number of solutions of (1) is the product of the numbers of solutions of (2) and (3) ; or :

$$\nu(NN', M_1M_1', M_2M_2', M_3M_3') = \nu(N, M_1, M_2, M_3)\ \nu(N', M_1', M_2', M_3')$$

if $NM_1M_2M_3$ is prime to $N'M_1'M_2'M_3'$.

This proves the multiplicative property of the function $\nu(N, M_1, M_2, M_3)$. A similar proof holds for the corresponding function defined in the same way for more than three arguments M.

THEOREM VI. *The function* $\nu(N, M_1, M_2, \ldots, M_r)$ *defined as the number of solutions of the equation*

$$c_1 + c_2 + \ldots + c_r = 0 \text{ mod } N,$$

where c_i *belongs to the same class mod* N *as* M_i, *is equal to*

$$\nu(N, g_1, g_2, \ldots, g_r),$$

where g_1 *is the g.c.d. and* g_r *the l.c.m. of* $M_1, M_2, \ldots, M_r$ *and* g_i *the g.c.d. of their l.c.m.'s* i *at a time.*†

For since the function ν is multiplicative, it is sufficient to prove the result when all the arguments are powers of a prime p ; *i.e.*, it is sufficient to prove the theorem for ν (p^n, $p^{k_1}, p^{k_2}, \ldots, p^{k_r}$). Since however ν is symmetric in

† $g_1, g_2, \ldots g_r$ were called the successive *g.c.d.*'s of $M_1, M_2, \ldots, M_r$ in my paper "on the Arithmetico-logical symmetric functions of *n* Attributes", *Proc. of the Ind. Acad. of Sciences.* The index of any prime p in g_i is the *i*th in ascending order of its indices in $M_1, M_2, \ldots, M_r$.

the arguments $M_1, M_2, \ldots, M_r$, we can rearrange $p^{k_1}, p^{k_2}, \ldots, p^{k_r}$ in the ascending order of indices without affecting the value of the function. This rearrangement is equivalent to replacing $p^{k1}, p^{k2}, \cdots, p^{k_r}$ by their successive g.c.d.'s. Thus the theorem is proved when the arguments are powers of a prime, and therefore for the general case.

Cor. If g_i' is the *g.c.d.* of g_i and N,

$$\nu(N, M_1, M_2, \ldots) = \nu(N, g_1, g_2, \ldots) = \nu(N, g_1', g_2' \ldots).$$

For the values of $g_1, g_2, \ldots$ are relevant to the value of ν, only through the classes mod N to which they belong.

THEOREM VII. $\nu\ (N, M_1, M_2, M_3) = \phi\left(\frac{N}{g_3}\right)\phi\left(\frac{N}{g_1}\right) \Pi\left(1 - \frac{1}{q-1}\right)$ or zero, *according as* $g_1 =$ *or* $\neq g_2$, *where* g_1, g_2, g_3 *are the g.c.d.'s with* N *of the successive g.c.d.'s of* M_1, M_2, M_3 *and the product extends over the prime factors* q *of* $\frac{N}{g_1}$ *which do not occur in* $\frac{g_3}{g_1}$.

For, $\nu(N, M_1, M_2, M_3) = \nu(N, g_1, g_2, g_3)$ is the number of solutions of

$$c_1 + c_2 + c_3 = 0 \mod N,$$

where c_i belongs to the class g_i $(i = 1, 2, 3)$; that is, of

$$k_1 + k_2 + k_3 = 0 \mod \frac{N}{g_1},$$

where k_1 is prime to $\frac{N}{g_1}$ and k_2, k_3 belong to the respective classes $\frac{g_2}{g_1}, \frac{g_3}{g_1}$ mod $\frac{N}{g_1}$. This congruence has evidently no solution if $g_2 \neq g_1$; if $g_2 = g_1$, by Theorem II, the number of solutions is $\phi\left(\frac{N}{g_3}\right)\phi\left(\frac{N}{g_1}\right) \Pi\left(1 - \frac{1}{q-1}\right)$ as stated.

Cor. If M_1, M_2, M_3 belong to the classes C_i, C_j, C_k respectively mod N, then $\nu\ (N, M_1, M_2, M_3) = \phi\left(\frac{N}{t_k}\right) \gamma_{ij}{}^k$. Hence

$$\gamma_{ij}{}^k = \frac{1}{\phi(N/t_k)} \cdot \phi(N/g_3) \cdot \phi(N/g_1) \ \Pi\left(1 - \frac{1}{q-1}\right).$$

THEOREM VIII.

$$\nu(N, M_1, M_2, \cdots, M_r) = \Sigma \frac{\nu(N, M_1, M_2, \cdots, M_k, t)\, \nu(N, M_{k+1}, \cdots, M_r, t)}{\phi\left(\frac{N}{t}\right)}$$

where the sum extends over all divisors t *of* N.

For, the solutions enumerated in $\nu(N, M_1, M_2, \ldots, M_r)$ are also the solutions of the simultaneous equations

$$c_1 + c_2 + \ldots + c_k = m(\text{mod N})$$

$$c_{k+1} + c_{k+2} + \ldots + c_r = -m \text{ (mod N) } (m = 1, 2,, N),$$

where c_i belongs to the same class as M_i. When m is a given number belonging to the same class as the divisor t of N, the number of solutions of these two equations is :

$$\frac{\nu\,(N, M_1, M_2, \ldots M_k, t)}{\phi\left(\frac{N}{t}\right)} \cdot \frac{\nu(N, M_{k+1}, \ldots, M_r, t)}{\phi\left(\frac{N}{t}\right)}.$$

Hence, when m varies over the $\phi\left(\frac{N}{t}\right)$ numbers of class (t), the number of solutions obtained is $\phi\left(\frac{N}{t}\right)$ times this number. By summing over all the divisors t, we get the result of the theorem.

V. The Class-Division of a Group.

THEOREM IX. *There exists a division of the elements of a group* G, *into classes which combine among themselves by the group operation, corresponding to every group* G_1 *of automorphisms of* G.

For, let each element of G with all the elements into which it is transformed by the automorphisms in G_1 be put into a class ; the classes thus formed combine among themselves by the group-operation. For if c_k an element of the class C_k occurs precisely t times in the set $C_i C_j$, then if g is any automorphism comprised in G_1, the element $g(c_k)$ must occur precisely t times in the set $g(C_iC_j) = g(C_i).g(C_j)$; that is to say, in the set C_iC_j. By proper choice of g, $g(c_k)$ can represent any element of the class C_k, which proves the theorem.

If G_2 is any subgroup of G_1, it is clear that the class-division corresponding to G_2 is obtained by a subdivision of the classes C corresponding to G_1. If G_1 is the group of inner automorphisms we obtain the class-division into conjugate sets and the associated Frobenius algebra of the group. If G_1 is the total group of automorphisms of G, the corresponding class-division is a *maximal* one, in the sense that every other class-division (*e.g.*, the division into conjugate sets of elements) arises by a subdivision of the classes corresponding to the maximal division. Thus the maximal division arises by grouping together certain conjugate sets of elements into classes. In certain cases, the maximal classes consist of all elements of the same order of the group. It will be seen presently that this is the case in Abelian groups. Whether this is the case in other classes of groups (for example, in groups of odd order) I am unable to say definitely.

An Abelian group has no inner automorphisms other than the identical automorphism. A cyclic group of order N is abstractly identical with the additive group of residue-classes mod N. The (outer) automorphisms of the cyclic group correspond to the multiplication of the residue-classes by a number prime to N. The class-division of the numbers mod N which we have discussed is precisely the maximal class-division which corresponds to the total group of automorphisms of the cyclic group. It is clear that in this division the elements of a class are all the elements of the group of a given order. This division can be obviously extended to any Abelian group.

THE RAMAN SPECTRA OF CRYSTAL POWDERS.

I. The Halides and Sulphate of Ammonium.

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1. *Introduction.*

In a recent communication to these *Proceedings*[1] the author gave a preliminary account of the Raman spectra of a few compounds belonging to the nitrogen group. The obvious incompleteness of the data reported therein for some of these substances—these are crystalline solids under ordinary conditions—as well as the importance of a detailed elucidation of their spectra from the standpoint of the electronic theory of valency was realised and emphasised in the same paper. In the meanwhile, a new technique has been developed by the author which has rendered it possible for the first time to photograph the *complete* Raman spectra of crystal powders, and even of amorphous substances with as much facility and elegance as in the case of liquids by the well-known method due to Prof. R. W. Wood. Although a brief report of the new technique and also of some of the results obtained have already appeared,[2] a short description of the exact experimental arrangement employed by the author and of certain improvements that have been effected subsequent to the publication of the notes referred to above are added in the next section. The present paper which is the first of a series deals with the results obtained in the case of NH_4F, NH_4Cl, NH_4Br, NH_4I, and $(NH_4)_2SO_4$ all of which have been studied in the solid state. All the chemicals excepting NH_4I were Kahlbaum's purest reagents; ammonium iodide was prepared from NH_3 and HI.

2. *Experimental: Technique of Complementary Filters.*

Although the powder technique for photographing the Raman spectra of crystalline solids originated by Menzies[3] and Bär[4] has been applied to the

1. R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 204.
2. R. Ananthakrishnan, *Curr. Sci.*, 1936, **5**, 131.
   R. Ananthakrishnan, *Nature*, 1936, **138**, 803.
3. A. C. Menzies, *Nature*, 1929, **124**, 511.
4. R. Bär, *Nature*, 1929, **124**, 692.

study of a variety of crystals, it is well known that at best only the strongest Raman lines can be recorded by this method. This is because of the powerful continuous spectrum that extends over the entire plate and obliterates all the fainter lines even when the duration of exposure is comparatively short. The origin of this continuous spectrum has been very often attributed to the continuous spectrum present in the mercury arc light itself, but attempts to get rid of it have hitherto been entirely futile. After some preliminary work, the present author soon realised that the continuous spectrum was actually due to the intense illumination in the interior of the spectrograph caused by the powerful light of the mercury arc reflected by the crystal faces. The difficulty was therefore successfully overcome by the selective absorption of the exciting line from the scattered light before the latter was admitted into the spectrograph.

The experimental technique will be sufficiently clear from Figs. 1*a* and 1*b*. Mercury arc light filtered by a *moderately strong solution of iodine in* CCl_4 falls on the crystal powder contained in the inner of the two concentric

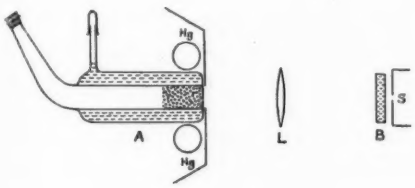

FIG. 1 (*a*).

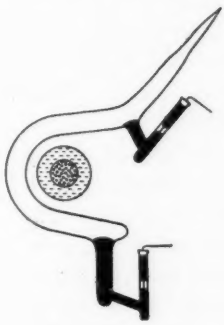

FIG. 1 (*b*).

tubes A. The transversely scattered light is collected by the lens L, and is focussed on the slit S of the spectrograph after it has passed through a glass cell B which contains a *solution of* $NaNO_2$ of suitable strength. Filter A, provided it be of sufficient strength and thickness (these can be easily adjusted) transmits freely λ 4046 of the mercury arc, which therefore serves as the exciting line while it practically absorbs the entire mercury spectrum to the longer wave-length side. Filter B, the concentration and thickness of which can also be varied, transmits the spectral regions to the longer wave-length side of λ 4046, while it has got a fairly sharp cut off to the shorter wave-length side starting from very near λ 4046. The exciting line is thus considerably weakened if not completely absorbed before the scattered light enters the spectrograph, and this procedure results in a vast improvement

in the technique of the photography of the Raman spectra of crystal powders. Indeed, exposures of duration comparable to that in the case of liquids are rendered possible, and the photographs so obtained reveal a corresponding wealth of detail and information in the case of every one of the crystal powders which the author has so far examined.

The above technique, however, fails to reveal the presence (if any) of Raman lines between $\Delta\nu = 1650$ and $\Delta\nu = 1760$ cm.$^{-1}$ because of the presence of the λ 4358 group of mercury lines in this region, which, although considerably enfeebled by the iodine filter are nevertheless recorded on the plate. A simple modification of the technique has been found to overcome this difficulty. A *very dilute solution of iodine in* CCl_4 is employed in place of the original strong solution. This freely transmits the mercury lines λ 4046 and λ 4358 which therefore function as the exciting lines, while *this filter has got the remarkable property of absorbing practically completely the* λ 4916 *group of feeble mercury lines as well as the powerful green line* λ 5461. The necessity and importance of cleaning up the λ 4916 region, particularly in working with crystal powders using λ 4358 excitation is only too well known, and although various filters have been suggested for this purpose, it appears that the above filter is the ideal one. When employing this filter, a *very dilute solution of* $KCrO_4$ serves as the filter B in front of the slit of the spectrograph.* Its concentration and thickness are so adjusted, that it absorbs the violet end of the spectrum up to λ 4358, suitably weakens the exciting line λ 4358 itself, and transmits freely the spectrum to the longer wave-length side of λ 4358. Thus two photographs taken first with a concentrated and then with a dilute solution of iodine in CCl_4 to filter off the exciting light with the corresponding complementary filters give the complete spectral details of the substance under investigation.†

The remarkable stability of the iodine filter apart from its other properties mentioned above renders it extremely useful in powder work as an efficient filter for the incident light. The solution of $NaNO_2$ has got a *sharp and steep* absorption edge near λ 4046 and so forms an efficient combination with the iodine filter. The absorption edge of the $KCrO_4$ solution is, however, not so sharp, but extends over a few hundred wave numbers ; it is therefore unsatisfactory for investigating Raman lines which fall close to the exciting line λ 4358.

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* The absorption band of $KCrO_4$ solution as given in the absorption chart in Prof. R. W. Wood's *Physical Optics*, 1934, p. 16, seems to be incorrect. Even for a dilute solution, the absorption extends beyond λ 4358.

† The technique ought to be extended to the green and yellow lines of the mercury arc so as to enable the investigation of coloured solids.

Unlike liquids and gases, increasing the depth of the illuminated column does not give a corresponding increase in intensity of the scattered light when working with crystal powders, and in practice, it is unnecessary to employ a depth exceeding a centimetre or two. Increased intensity of the scattered light can only be secured by increasing the illumination of this short column, and this is realised by the use of a circular arc of the type shown in Fig. 1*b* and placing the Raman tube containing the crystal powder at its centre. Such an arc is easily made out of a tube of pyrex glass about a centimetre in diameter, and works continuously for any length of time when cooled by a stream of air from a fan which serves at the same time to prevent the filter A as well as the crystal powder from getting unduly heated.

3. Results.

Photographs of the Raman spectra obtained by the new technique are reproduced in Fig. 2. The following table gives the frequency shifts, relative intensities (visual) and nature of the observed Raman lines or bands for the substances studied in the present paper :—

s = sharp
b = broad
d = diffuse

k = λ 4046
i = λ 4078
e = λ 4358
} Exciting lines.

TABLE I.

NH_4F	NH_4Cl	NH_4Br	NH_4I	$(NH_4)_2SO_4$
?	1398 (k) 1s 1424 (k) 0d	1395 (k) 1	?	(984) (k) 6s [SO_4^{--} ion]
?	1700 (e) 3s 1750 (e) 1s	1690 (e) 6s	1665 (k) ? 0	
	2009 (k, e) 1bd	2000 (k) ? 00d		
2262 (k) ½d				
2820 2870 (k) 3bd (incompletely resolved)	2813 (k, e) 3bd	2800 (k, e) 3d	2780 (k) 0d	
	3040 (k, e) 8bd	3025 (k, e) 8bd		
3088 (k) 2bd			3100 (k, e) 4bd	
	3142 (k, e) 5bd	3126 (k, e) 6bd		3160 (k) ½bd

4. Discussion of Results.

The Raman spectra of the ammonium salts are of great interest because apart from the question of the constitution of the ammonium ion which is a

problem of interest and importance, one might, perhaps, expect to gain some insight into the nature of the rotational motion of molecules in crystals, the existence of which has been predicted by Pauling[5] from theoretical considerations. Thus, in the case of the ammonium salts, the $[NH_4]^+$ ion is supposed to be executing free rotation at ordinary temperatures, the rotational motion gradually subsiding and giving place to angular oscillations of diminishing amplitude as the temperature is progressively lowered.

The Raman[6] and infra-red absorption[7] spectra of the ammonium salts in the crystalline state have attracted a good deal of attention. The results of the earlier workers on the Raman spectra are incomplete, presumably because of the difficulty experienced by them in obtaining good photographs. Recently, Holmes[6] has succeeded in recording the complete Raman spectrum of NH_4Cl by working with a single crystal of the substance the preparation of which appears to have taken him nearly a month. While Menzies and Mills[6] came to the conclusion that many of the observed facts relating to crystalline NH_4Cl and NH_4Br could be explained by assuming a tetrahedral structure for the $[NH_4]^+$ ion, Holmes concluded that his results tended to show that the symmetry of the $[NH_4]^+$ ion in crystalline NH_4Cl departs from the usually assumed tetrahedral structure. The object of the present investigation was to make a detailed comparative study of the Raman spectra of all the four ammonium halides at room temperature. Such an investigation is lacking and is obviously necessary before any definite conclusions can be drawn.

(1) *NH_4Cl and NH_4Br.*—We shall consider the Raman spectra of these salts together because, it is known from X-ray work[8] that at room temperature both ammonium chloride and ammonium bromide possess the caesium-chloride structure, (body centred cube) each ammonium ion being surrounded by eight halogen ions at the corners of a cube. The following tables give a comparison between the Raman and infra-red absorption frequencies of these two substances at room temperature.

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5. L. Pauling, *Phys. Rev.*, 1930, **36**, 430.

6. C. Schaefer, F Matossi and H. Aderhold, *Z. f. Phys.*, 1930, **36**, 430.
A. Kastler, *Bull. Soc. Chim. France*, 1932, **51**, 728.
F. T. Holmes, *Phys. Rev.*, 1932, **41**, 389.
I. R. Rao and C. S. Rao, *Z. f. Phys.*, 1934, **88**, 127.
A. C. Menzies and H. R. Mills, *Proc. Roy. Soc.*, A, 1935, **148**, 407.
F. T. Holmes, *Jour. Chem. Phys.*, 1936, **4**, 88.

7. O. Reinkober, *Z. f. Phys.*, 1921, **5**, 192.
L. Wilberg, *Z. f. Phys.*, 1930, **64**, 304.
R. Pohlman, *Z. f. Phys.*, 1932, **79**, 394.

8. See R. W. G. Wyckoff, *The Structure of Crystals*, 1931, p. 227.

TABLE II. NH_4Cl.

Raman			Infra-red		
Menzies and Mills (1935)	Holmes (1936)	Author (1937)	Pohlman* (1932)	Wilberg (1930)	Reinkober (1921)
1400	1407 (2) (unresolved doublet)	1398 (1s) 1424 (0d)	1413 (6) 1424 (2)	1415 1436	1415
1712 1758	1709 (5) 1768 (2)	1700 (3s) 1750 (1s)	1773 (4)	1767	1767
	2010 (2)	2009 (1bd)	.. ..	2020 2247	2020 ..
			2353	2353	2353
	2824 (7)	2813 (3bd)	2857 (2)	2825	2857
3040	3041 (20)	3040 (8bd)	3059 (6)	3012	3087
3163	3146 (15)	3142 (5bd)	3164 (8)	3106	
	(3232) (3303)				

TABLE III. NH_4Br.

Raman			In-frared	
Kastler (1932)	Menzies & Mills (1935)	Author (1937)	Pohlman* (1932)	Reinkober (1921)
	1380 1420	1395 (1)	1408 (10) 1439 (2)	1408
	1689	1690 (6s)	1730 (4)	1694
		2000 (?) (00d)	 2353	2041 2326
2810		2800 (3d)	2833 (2)	....
3030	3032	3025 (8bd)	3049 (5)	3106
3130	3140	3126 (6bd)	3154 (8)	

*The relative intensities of infra-red absorption given in this column are visual estimates from the absorption curves given by Pohlman.

If, as it appears justifiable to conclude, it is assumed that all the Raman frequencies observed in the case of these two ammonium halides are due to the $[HN_4]^+$ ion, then one has to identify nearly six distinct frequencies as those appertaining to this ion in these crystals. These lie in the neighbourhood of 1400, 1700, 2000, 2800, 3000 and 3100 cm.$^{-1}$ respectively. The 1400 frequency is faint but sharp in the chloride and is accompanied by a diffuse companion. The corresponding frequency is faint but somewhat more diffuse in the bromide. The 1700 frequency is strikingly different in the two cases, a feature which has not been noticed before. It is sharp and very intense in the bromide, but is less intense and is split up into two components in the chloride. There is no such difference in the case of the corresponding infra-red absorption. The frequency $\Delta\nu \sim 2000$ is a diffuse band in the case of NH_4Cl; the presence of the corresponding band in the spectrum of the bromide is uncertain. It might be noted that the Raman spectrum of the hydrazinium ion $[N_2H_6]^{++}$ in crystalline $N_2H_4 \cdot 2HCl$ shows a band in exactly the same position. The remaining three frequencies are all diffuse bands and present more or less a similar appearance in the two cases. Of these three, the one at 2800 shows an asymmetric structure. It has got a fairly sharp edge towards the side of the exciting line, but is diffuse towards the other side. It is also less intense than the other two bands which are the most intense in the whole spectrum. Of these two, the band of lesser shift is more intense than the other, the difference in intensity being more conspicuous in the chloride than in the bromide. It might be of interest to mention that when employing the technique of complimentary filters, these two bands can be seen very clearly with the naked eye as soon as the complementary filter B is brought in front of the slit of the spectrograph, but when it is removed, the bands are lost in the general illumination.

Holmes has given for NH_4Cl two other frequencies 3232 and 3300 which he calls subsidiary frequencies of the $[NH_4]^+$ ion. When employing λ 4046 excitation, the author has observed on his plates two faint bands following the two intense ones mentioned above. Careful measurement and intensity considerations show that these can be regarded as the corresponding λ 4078 excitation, so that the author is unable to confirm the reality of these bands.

(2) *NH_4I.*—The crystal structure of this substance at room temperature is of the rocksalt type, each ammonium ion being surrounded by six equidistant halogen atoms. At low temperatures, the ammonium iodide lattice changes over to the caesium chloride structure so that it becomes isomorphous with the chloride and the bromide. At higher temperatures, the chloride and the bromide are transformed to the rocksalt structure. Thus the three ammonium halides exhibit polymorphism.

Ammonium iodide prepared from NH_3 and HI was coloured pale yellow but the crystals became perfectly colourless on repeated washing with acetone as recommended by Menzies and Mills. Two separate photographs were obtained in the manner explained in Section 2, but the spectrum in either case was weaker than that of the chloride or of the bromide. However, since the background was quite clear, the corresponding frequencies even if only faintly present could not have escaped notice.

As can be seen from Table I, the Raman spectrum of NH_4I at room temperature is very different from the spectra of the other two halides considered above. While the chloride and the bromide show two strong bands in the 3000 region, the spectrum of the iodide shows only a single diffuse band in this region. Its position (3100 cm.$^{-1}$) is somewhat midway between the above two bands. The band near 2800 appears to be present in the iodide, although its relative intensity has gone down considerably. The frequency near 1700 is doubtful, and in any case is very much less intense than the corresponding frequency for the chloride or the bromide. The band near 2000 is absent; the frequency near 1400 is probably too feeble to be recorded.

The infra-red frequencies of NH_4I at room temperature observed by Reinkober are 3106 (strong), 2342 (weak), 2000 (doubtful), 1667 (doubtful) and 1398 (strong). Menzies and Mills have observed two frequencies 3021 (strong) and 1662 in the Raman spectrum of NH_4I at $-50°$ C., when its crystal structure is of the caesium chloride type.

(3) *NH_4F.*—Crystals of NH_4F belong to the hexagonal system (wurtzite type) and do not exhibit polymorphism as the crystals of the other three halides. The substance investigated was Kahlbaum's analytical reagent and contained as per specification 5% of the double salt $NH_4F \cdot HF$. It attacks glass, but there was no difficulty in photographing the spectrum in the usual manner. Only λ 4046 excitation was employed and the spectrum thus obtained was much less intense than in the case of the other halides in spite of comparable conditions of illumination and exposure. Comparison with the infra-red frequencies observed by Reinkober is given below:

Raman	3088 (2bd)	2870 } (3bd) 2820 }	2262 ($\frac{1}{2}$d)		?	?
Infra-red	..	2857	2222	2000	1667 (?)	1495

(4) *$(NH_4)_2SO_4$.*—The crystal structure of ammonium sulphate is orthorhombic. The Raman spectrum of the ammonium ion was extremely feeble

in this case. Barring the totally symmetric vibration frequency of the SO_4^{--} ion, which was strongly recorded, the plate showed only a very diffuse band with a frequency shift of approximately 3160 cm.$^{-1}$ We see that the anion in this case has a profound influence on the vibrations of the ammonium ion. Pohlman's infra-red measurements also reveal a similar influence.

5. Conclusion.

From the preceding section it is clear that the Raman spectrum of the ammonium ion in the case of crystalline ammonium salts is dependent intimately upon the crystal structure as well as upon the nature of the anion. It follows therefore that a satisfactory and unique interpretation of the observed results can only be obtained if we consider the vibrations of the ammonium ion in its crystalline environment. The chloride, the bromide and the iodide are from this standpoint the simplest because of the comparatively simple crystal structure of the salts and also because the anion being monatomic cannot give rise to vibrational frequencies of its own. But even in these cases, the spectral facts do not admit of a simple interpretation.

Taking first the chloride and the bromide, we see that in spite of the strong resemblance between their spectra, there are at the same time differences which cannot be ignored. Judging merely from the number of frequencies, one might conclude, as Holmes did in the case of NH_4Cl, that the $[NH_4]^+$ ion in these crystals has not got the symmetry of a regular tetrahedral molecule such as CH_4. Indeed, there is very little comparison between the spectra of these crystals and the Raman spectrum of methane.

Holmes investigated the Raman spectrum of NH_4Cl at high temperature when its crystal structure is of the rocksalt type. He found that in place of the two bands in the 3000 region observed in the spectrum at ordinary temperatures, there was only a single broad and very intense band, the frequency shift of which was found to be 3102 cm.$^{-1}$ Practically all the other Raman frequencies observed in the spectrum at ordinary temperature were also present in the spectrum of the high temperature modification of the chloride, but his results show a distinct fall of intensity for the 1700 and 2800 Raman shifts. These facts suggest a broad resemblance between the Raman spectrum of NH_4I at room temperature and that of NH_4Cl at high temperatures when they both possess the same crystal structure.

Menzies and Mills have tried to give an explanation of their results on the Raman spectra at room temperature as well as at low temperatures, as also of many peculiar and interesting properties such as anomalous heat capacity, piezo-electric behaviour (NH_4Cl), double refraction (NH_4Br), etc., shown by crystalline NH_4Cl and NH_4Br at low temperatures by basing

themselves on the tetrahedral model of the ammonium ion—as suggested by the crystal structure of these halides—and by adopting the view put forth by Pauling that above a certain transition temperature (about – 30°C.) rotation of the $[NH_4]^+$ ion sets in in the crystal lattice of these salts. Thus, according to these authors, the following comparison can be drawn between the fundamental vibrational frequencies of $[NH_4]^+$ and CH_4.

	Single ν_1	Doubly degenerate ν_2	Triply degenerate	
			ν_3	ν_4
CH_4	2915	1520	3022	1304
$[NH_4]^+$	3043	1712	3123	1403

One important feature of the spectra of crystalline NH_4Cl and NH_4Br which has not received adequate emphasis by the previous workers might be pointed out in this connection. We see from Tables II and III that practically *all the Raman frequencies of these two substances have their analogues in the corresponding infra-red absorption spectra.* This seems to be true also for the fluoride and the iodide although the infra-red spectra of these two substances have not been so thoroughly investigated as those of the other two halides. This result is indeed very significant because it is entirely at variance with what we should expect for a regular tetrahedral molecule. Whether this result indicates an actual departure of the $[NH_4]^+$ ion from the symmetry of a regular tetrahedron can only be decided after the influence of the electric field of the surrounding halogen ions on the vibrations of the $[NH_4]^+$ ion has been carefully considered.

Some other points that come out of the present investigation might also be mentioned. The Raman band near 2800 occurs in the spectra of all the four halides. It might be the octave of the 1400 Raman frequency, but if this were so we have the somewhat strange and interesting result that the octave in all cases is very much stronger than the fundamental. It is also not improbable that at least in the chloride and the bromide of ammonium at room temperature, there is an accidental degeneracy ($1400 + 1700 \backsimeq 3100$) which causes the splitting of the 3100 frequency into the two observed components. A more comprehensive study of the Raman spectra of all the ammonium halides covering a wide range of temperature is perhaps necessary before any definite conclusions can be drawn on the constitution of the ammonium ion. There is, however, little doubt that the crystalline

field has a large influence on its vibrations and presumably also on its actual configuration in the crystal lattice.

The author's respectful thanks are due to Professor Sir C. V. Raman for his kind interest and suggestions in the course of the present work.

Summary.

The paper describes a new technique which has been developed by the author for photographing the Raman spectra of crystal powders. It consists essentially in employing a fairly monochromatic beam for excitation, and absorbing the exciting line from the scattered light before the latter enters the spectrograph, and involves thus the use of a pair of complementary filters. The new technique enables for the first time to obtain Raman spectrograms of crystal powders which are as elegant and rich in detail as those of liquids. The Raman spectra of NH_4F, NH_4Cl, NH_4Br, NH_4I and $(NH_4)_2SO_4$ in the crystalline state at room temperature have been examined by this method. The Raman spectrum of the ammonium ion shows a pronounced dependence upon the crystal structure of the salt as well as upon the nature of anion. The spectra of crystalline NH_4Cl and NH_4Br at room temperature are particularly intense, and comprise about six distinct frequencies. These crystals are isomorphous at this temperature and there is a striking general resemblance between their spectra in spite of individual differences. All the Raman frequencies of the ammonium ion in these two substances have their analogues in the infra-red absorption spectra. This result is very significant and although it suggests *a priori* the lack of tetrahedral symmetry for the $[NH_4]^+$ ion, it is pointed out that the influence of the crystalline environment on the vibrations of the ion has to be carefully considered before any definite conclusions are drawn. The spectra of NH_4I and NH_4F are weaker than and differ from those of the other two halides. This might be due partly to the fact that their crystal structure at room temperature is different from that of the other two halides. The Raman spectrum of the ammonium ion is extremely feeble in the case of $(NH_4)_2SO_4$ which shows the enormous influence of the complex anion on the vibrations of $[NH_4]^+$.

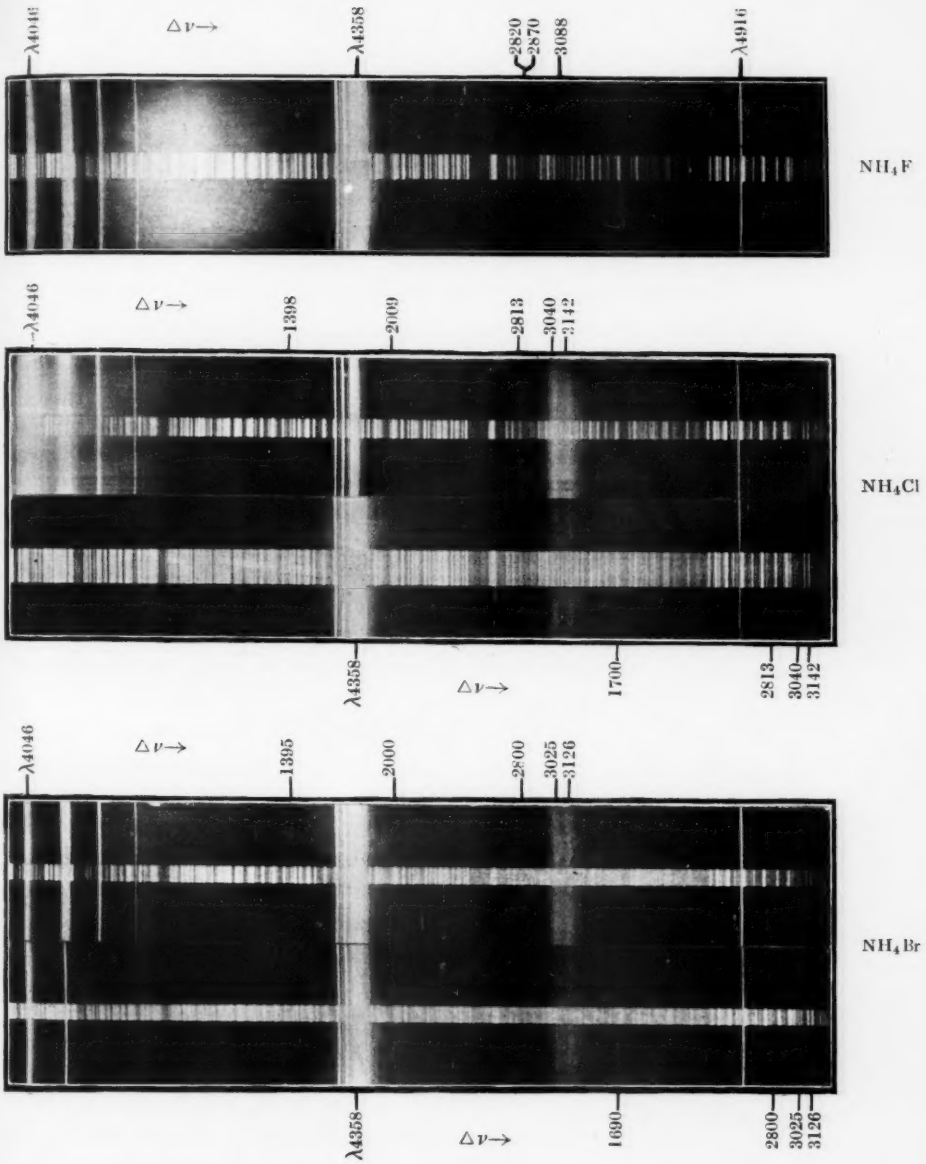

FIG. 2. Raman spectra of crystalline ammonium halides.

THE RAMAN SPECTRA OF CRYSTAL POWDERS.

II. The Chlorides and Sulphates of Hydroxylamine and Hydrazine.

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1. Introduction.

In previous communications[1] the author has described a new method for obtaining Raman spectrograms with crystal powders. The present paper reports the results obtained by this method in the case of hydroxylammonium and hydrazinium ions, and forms the sequel to the investigation of the ammonium group published separately in these *Proceedings*.[2] Crystals of the chlorides and sulphates of hydroxylamine and hydrazine have been experimented with, and the results are compared with the Raman spectra of the aqueous solutions of these substances investigated on a former occasion.[3]

2. Experimental.

The crystals employed were Kahlbaum's purest chemicals. The exciting line was λ 4046 of the mercury arc and the duration of exposure amounted to about 72 hours in each case. A Fuess spectrograph was employed in the investigation.

3. Results.

The following table gives the Raman frequencies with the estimated (visual) relative intensities and observed structural characters :

s = sharp	k = λ 4046	Exciting lines
b = broad		
d = diffuse	i = λ 4078	

[1] R. Ananthakrishnan, *Curr. Sci.*, 1935, **5**, 131.
R. Ananthakrishnan, *Nature*, 1936, **138**, 803.
R. Ananthakrishnan, *Proc. Ind. Acad Sci.*, **A**, 1937, **5**, 76.

[2] R. Ananthakrishnan, *Loc. cit.*

[3] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **A**, 1936, **4**, 204.

TABLE I.*

$NH_2OH \cdot HCl$	$(NH_2OH)_2 \cdot H_2SO_4$	$HCl \cdot NH_2 \cdot NH_2 \cdot HCl$	$N_2H_4 \cdot H_2SO_4$
			(465) (k) ½d
			(614) (k) 0
	(978) (k, i) 8s		(965) (k, i) 10s
999 (k, i) 15s	*1000* (k) 6s	*1024* (k, i) 10s	*1050* (k, i) 8s
	1012 (k, i) 8s		
	1065 (k) ½d		
1168 (k) ½s	? (1117) (k) ½d		
1463 (k) ½s			
1493 (k) 6s	1498 (k) ½d		
1551 (k) ½s	1547 (k) 1d	1519 (k) 3	1537 (k) 1d
1571 (k) ½s	1596 (k) 1d	1594 (k) 1	1608 (k) ½d
		2009 (k) 1bd	
2630 (k) 1d		2544 (k) 3bd	
2763 (k) ½d	2743 (k) ½bdd	2610 (k) 2	
2927 (k) 3b	2962 (k) 3bd	2660 (k) 1	
3005 (k) 4bd		2735 (k) 3bdd	
3045 (k) 3bd		2805 (k) 1d	
3173 (k) 2bd	3126 (k) 2bdd	2865 (k) 2d	
(double band)	3250 (k) ½bdd	2937 (k) 2d	
		2980 (k) 2d	
		3030 (k) 0d	
		3075 (k) 0d	3094 (k) 1bbdd
		3183 (k) ? 00d	

* Frequencies enclosed in brackets ( ) are due to the internal vibrations of the $(SO_4)^{--}$ ion.

4. Discussion.

(1) *$NH_2OH \cdot HCl$ and $(NH_2OH)_2 \cdot H_2SO_4$.*—The Raman spectra of the aqueous solutions of these substances have been already reported by the author. Excluding the water bands in the 3 μ region, the aqueous solution of $NH_2OH \cdot HCl$ showed a sharp and intense line shifted by 1008 cm.$^{-1}$ and a weak, broad and diffuse band at about 2960 wave numbers. Practically identical results were obtained for the aqueous solution of the sulphate, the spectrum of which showed in addition the characteristic frequencies of the $(SO_4)^{--}$ ion as well. Although attempts were made on that occasion to photograph the spectrum of crystalline $NH_2OH \cdot HCl$, the photograph obtained was very unsatisfactory, and showed only a single shift at 1000 cm.$^{-1}$

Compared with these results, an amazing wealth of detail is revealed by the spectrograms of the crystalline salts photographed by the new

technique. We shall first consider the spectrum of $NH_2OH \cdot HCl$ crystals. Since the anion $\overline{Cl}$ is monatomic, it might be justifiable to assume that all the Raman frequencies observed in the spectrum of this substance arise from the vibrations of the cation, the hydroxylammonium ion, $[H_3N \cdot OH]^+$. We might therefore expect a certain broad similarity with the Raman spectrum of methyl alcohol, $H_3C \cdot OH$, although it ought to be borne in mind that deviations are bound to exist because of the influence of the electric field of the neighbouring ions in the crystal lattice.

TABLE II.

$[H_3N \cdot OH]^+$	999 (15s)	1168 ($\frac{1}{2}$s)	1463 ($\frac{1}{2}$s) 1493 (6s) 1551 ($\frac{1}{2}$s) 1571 ($\frac{1}{2}$s)	2630 (1d) 2763 ($\frac{1}{2}$d) 2927 (3b) 3005 (4bd) 3045 (3bd) 3173 (2bd) (double band)	?
$H_3C \cdot OH$	1032 (10b)	1109 (1b) 1166 (1b)	1454 (5b)	2729 (1) 2833 (6b) 2944 (4) 2980 (2)	3430 (4bd) (O–H band)

The frequencies of the $[H_3N \cdot OH]^+$ ion may be divided into three groups. The intense sharp line at 999 cm.$^{-1}$ has its origin primarily in the N–O vibration. There is a small but definite increase in this frequency in the case of the aqueous solution.[4] Between 1000 and 1600 cm.$^{-1}$ we get five Raman frequencies of which the one at 1493 is by far the most intense. From the vast mass of experimental data which we now possess on the Raman spectra of molecules, we can conclude that these frequencies are due to the N–H flextural or deformation vibrations. It is surprising that the frequency 1493 which comes out strongly in the crystal photograph is practically washed out in the aqueous solution of the chloride. The third group of frequencies above 1600 represents the N–H valence oscillations. Their diffuseness is due in all probability to the crystalline electric field which presumably exerts a profound influence on these vibrations. Perhaps, rotation of the ion in the crystal lattice[5] also contributes towards the

[4] R. Ananthakrishnan, *Loc. cit.*

[5] L. Pauling, *Phys. Rev.*, 1930, **36**, 430.

observed diffuseness of the N–H bands in the spectra of these crystals. The relative sharpness of the Raman lines arising from the flextural oscillations as contrasted with the diffuseness of those arising from valence oscillations appears to be a general feature of the spectra of the crystalline halides of ammonium, hydroxylamine and hydrazine. Investigation of these substances at low temperatures might enable us to gain a better understanding of this phenomenon. Indeed, the complex and diffuse structure of these N–H bands finds a parallel in the O–H frequencies observed in the case of crystals containing water of crystallisation. A systematic investigation of the latter has been engaging the author's attention for some time past, and the results will be published in the near future.

Judging from the number of the N–H valence and deformation frequencies, it appears likely that the symmetry of the $[H_3N \cdot OH]^+$ ion in the crystal lattice of $NH_2OH \cdot HCl$ is inferior to that of the $H_3C \cdot OH$ molecule. It is, for instance, extremely doubtful that the NH_3 group in the ion has the symmetry C_{3v} of the CH_3 group. Whether this want of symmetry is connected with the nature of the N–H bonds or is brought about by external perturbation remains an open question. As far as the author is aware, neither the X-ray crystal structure nor the infra-red absorption frequencies of hydroxylamine hydrochloride is available. It will be noticed that the O–H oscillation which comes out as a broad and intense band in the spectrum of methyl alcohol does not appear in the spectrum of the $[H_3N \cdot OH]^+$ ion.

The spectrum of crystalline $(NH_2OH)_2 \cdot H_2SO_4$ shows at a glance the profound influence of the anion $(SO_4)^{--}$ on the vibrations of the cation. The whole spectrum is very much weaker, and the N–H frequencies are considerably more diffuse than in the case of the chloride. A strange and surprising result is that in place of the single sharp and intense line ν(N–O) $= 999$ cm.$^{-1}$ observed in the Raman spectrum of the crystalline chloride, a sharp doublet separated by 12 wave numbers appears in the spectrum of the crystalline sulphate. As already pointed out, the aqueous of solution of the sulphate shows only a single sharp line in this position, so that we have here a striking illustration of the influence of oppositely charged ions on their characteristic vibrations in the crystal lattice. The δ(N–H) frequency at 1493 which is quite intense in the spectrum of the chloride is considerably enfeebled in the case of the sulphate.

(2) *$N_2H_4 \cdot 2HCl$ and $N_2H_4 \cdot H_2SO_4$.*—Crystalline $N_2H_4 \cdot 2HCl$ as well as its aqueous solution examined by the author on a former occasion gave only very meagre results. The new technique, however, has yielded for the crystalline salt a spectrum comprising no less than 15 Raman frequencies.

The photograph in the plate shows the multitude of diffuse Raman bands exhibited by this substance in the spectral region above 2500 cm.$^{-1}$.

As in the case of $NH_2OH \cdot HCl$, we shall assume that all the observed frequencies in the case of $N_2H_4 \cdot 2HCl$ arise from the vibrations of the cation, in this case the hydrazinium ion $[H_3N \cdot NH_3]^{++}$. Some similarity with the Raman spectrum of ethane might then be expected.

TABLE III.

$[H_3N \cdot NH_3]^{++}$	1024 (10s)	1519 (3) 1594 (1)	2009 (1bd) 2544 (3bd) 2610 (2) 2660 (1) 2735 (3bdd) 2805 (1d) 2865 (2d) 2957 (2d) 2980 (2d) 3030 (0d) 3075 (0d) 3183? (00d)
$H_3C \cdot CH_3$ (gas)*	993 (3)	1344 (0)	2744 (2) 2778 (0) 2899 (6) 2940 (1) 2955 (7) ....

* C. M. Lewis and W. V. Houston, *Phys. Rev.*, 1933, **45**, 903.

The most intense line in the spectrum of hydrazine hydrochloride is the one at 1024 cm.$^{-1}$ which represents the N–N oscillation. The two frequencies 1519 and 1594 and perhaps also the broad band at 2009 represent δ(N–H) oscillations. The remaining frequencies which count nearly a dozen may be connected with the numerous other vibrations of the hydrazinium ion which are due principally to the stretching of the N–H bonds. In spite of the formal analogy with ethane, it would seem highly doubtful whether the $[N_2H_6]^{++}$ ion has the same symmetry as that of the ethane molecule. Judging merely from the number of frequencies, one is tempted to conclude that the NH_3 groups in this ion have not got the symmetry of the CH_3 groups in ethane; but such a conclusion is by no means decisive.

When we examine the spectrum of $N_2H_4 \cdot H_2SO_4$ we find once again the marked influence of the sulphate ion on the vibrations of the $[N_2H_6]^{++}$ ion.

The frequency of the symmetric vibration of the hydrazinium ion shifts from 1024 in the chloride to 1050 in the sulphate. What is more remarkable still is the practically complete disappearance of all the frequencies beyond 2000 cm.$^{-1}$, probably because of their lesser intensity and enhanced diffuseness. The δ (N–H) frequencies are still recognisable as very diffuse bands.

(3) *Disappearance of the N–H bands in aqueous solutions.*—From an investigation of the near infra-red absorption spectra as well as the Raman spectra of aqueous solutions of various nitrogen derivatives, Freymann, Freymann and Rumpf[6] have recently come to the conclusion that the N–H bands in the 3 μ region disappear completely when the covalency of nitrogen changes from three to four. Thus, these bands were quite intense in the case of aqueous solutions of ammonia, amines, etc., whereas aqueous solutions of NH_4Cl, $NH_2OH \cdot HCl$, $N_2H_4 \cdot 2HCl$ failed to show any trace of these bands. The author's observations on the Raman spectra of the aqueous solutions of these salts lend support to the view that there is a considerable weakening of the N–H bands of all these substances when they are dissolved in water. It is, however, difficult to assert with certainty that they disappear altogether. In fact, as has been already remarked, the aqueous solution of the salts of hydroxylamine show a broad and diffuse band at about 2960 wave numbers. We have also seen that the N–H bands in all these compounds are very diffuse even in the crystals, and are considerably influenced by a complex anion such as $(SO_4)^{--}$. Apart from a probable influence of the solvent on the N–H bands, aqueous solutions of these salts are generally somewhat fluorescent, and the consequent background combined with the broad and intense water band in the 3 μ region might easily mask the presence of the faint N–H bands in the Raman spectra of these solutions.

5. *Conclusion.*

A definite result coming out for the first time from the author's investigation of the Raman spectra of crystalline NH_4Cl, $NH_2OH \cdot HCl$ and $N_2H_4 \cdot 2HCl$ is that the N–H frequencies in these compounds have a very wide range extending roughly from about 2500 to 3200 wave numbers, with a concentration of intensity near about 3000 wave numbers. This range is practically identical with that of the C–H frequencies observed in organic compounds. A result of some significance is also brought out when we compare the N–H frequencies observed in these compounds with those observed in the case of ammonia and the amines wherein nitrogen is trivalent.

[6] Mme. M. Freymann, M. M. R. Freymann and P. Rumpf, *Jour. de Phys.*, 1936, **7**, 30.

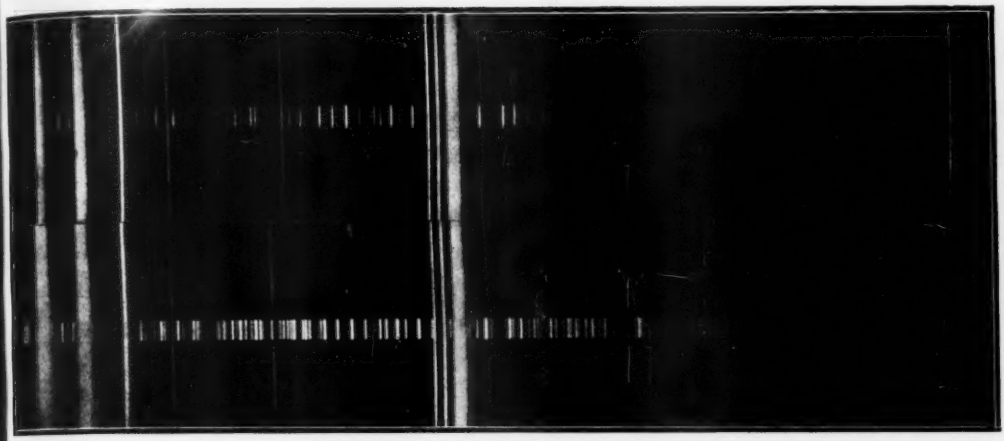

FIG. 1. Raman spectra of crystal powders.
(i) $N_2H_4 \cdot 2\,HCl$; (ii) $N_2H_4 \cdot H_2SO_4$.

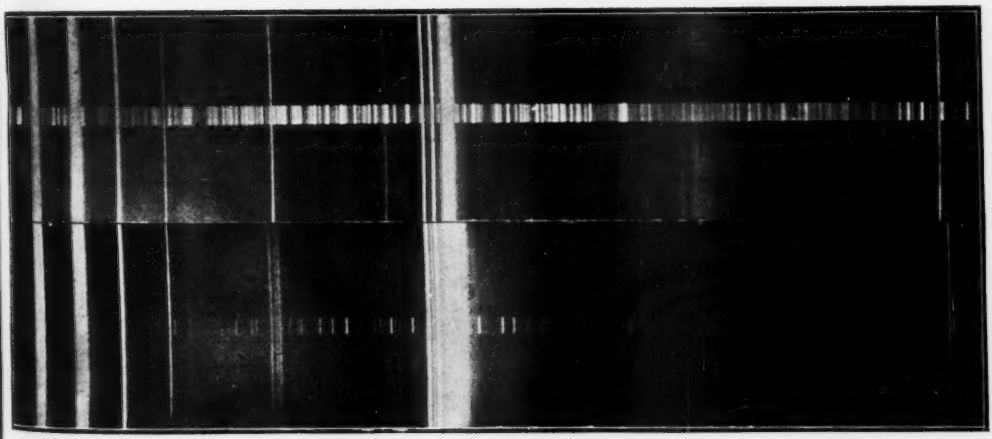

FIG. 2. Raman spectra of crystal powders.
(i) $NH_2OH \cdot HCl$; (ii) $(NH_2OH)_2 \cdot H_2SO_4$.

In all compounds of the latter type, the N–H frequencies always lie between 3200 and 3500, with a concentration of intensity round about 3300. We thus come to the conclusion that *when the covalency of nitrogen changes from three to four, there is a definite lowering of the N–H frequency, in other words, a weakening of the N–H bond.* We have an analogous result in the case of organic compounds. Aromatic C–H frequencies always exceed 3000, while the C–H frequencies of saturated aliphatic compounds containing no double bonds lie between 2500 and 3000 wave numbers.

The author's respectful thanks are due to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

The paper reports the Raman spectra of crystalline $NH_2OH \cdot HCl$, $(NH_2OH)_2 \cdot H_2SO_4$, $N_2H_4 \cdot 2HCl$, and $N_2H_4 \cdot H_2SO_4$, photographed by the powder technique recently described by the author. The spectra of the chlorides reveal many interesting features relating to the vibrations of the hydroxylammonium and hydrazinium ions, the most characteristic of which is perhaps the multiplicity and diffuseness of the N–H bands whose frequencies range roughly from 2500 to 3200 wave numbers. The N–H bands are considerably weakened and are very much more diffuse in the case of the sulphates. There is a probable structural similarity between the $[H_3N.OH]^+$ ion and $H_3C \cdot OH$ and $[H_3N \cdot NH_3]^{++}$ and $H_3C \cdot CH_3$ although the spectra of the ions are very much more complicated than those of the corresponding organic molecules. From a comparison of the Raman spectra of tri- and pentavalent nitrogen derivatives, it is found that there is a definite lowering of the N–H frequencies in the compounds of the latter class. It is therefore concluded that when the covalency of nitrogen changes from three to four, there is a definite weakening of the N–H bond.

[*Note added in proof*:—Since this paper was sent to the Press, a paper of K. W. F. Kohlrausch (*Mon. f. Chem.*, 1936, **68**, 349) containing a discussion of the Raman spectrum of hydrazine, $H_2N.NH_2$ has come to the author's notice. For pure hydrazine in the liquid state, Kohlrausch has found the Raman frequencies 876 (4*b*), 1108 (5*b*), 3181 (10*b*), 3263 (7*b*) and 3332 (7*b*). On the analogy with molecules such as $H_3C.CH_3$, $H_3C.NH_2$, $H_3C.OH$, etc., Kohlrausch has concluded that the frequency 876 should correspond to the N–N vibration of the hydrazine molecule. According to him, this means that the N-N binding in hydrazine is weaker than the C–C, C–N and C–O bindings. The author's work shows that such a result is highly improbable. The N–N frequency observed for the crystalline salts of hydrazine as well as for their aqueous solutions (pentavalent nitrogen) is greater than 1000 $cm.^{-1}$; the corresponding frequency might be expected to be somewhat higher in the case of pure hydrazine (trivalent nitrogen), so that it would seem justifiable to identify 1108 as the N–N frequency in this case. This would mean that the N–N binding in hydrazine is not weaker than the C–C, C–N or C–O bindings.]

DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part I. Gold Sols.

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1. Introduction.

The problem of the diffraction of light by spherical conducting particles was dealt with rigorously on the basis of the electromagnetic theory by G. Mie[1] in a well-known paper. He developed formulæ for the scattering and absorption of light by colloidal solutions under the assumption that the refractive index and the absorption coefficient of the colloidal particles possess the same values as those of the metal in bulk. In this theoretical paper the colour phenomena of metals in the colloidal state, especially of gold sols, have been beautifully explained by him. According to this theory small gold particles give ruby red solutions whereas large ones give blue solutions. This accords well with the experimental observations. Further, Mie's theory indicates regarding the state of polarisation of the scattered light that when the beam incident horizontally is unpolarised, the light scattered in the transverse horizontal direction by the particles in the colloidal state will be perfectly polarised with vibrations vertical if the size of the particles is the order of molecular dimensions, and will be imperfectly polarised only if the size is comparable with the wave-length of light. Moreover, if the incident beam is polarised with vibrations vertical or horizontal, the light scattered transversely in the horizontal direction should be completely polarised with its vibrations vertical or horizontal respectively. Steubing[2] has, however, shown experimentally that in gold sols the transversely scattered light is not completely polarised even when the incident light is plane polarised. This fact of observation does not find an explanation in Mie's theory.

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[1] G. Mie, *Ann. der Phys.*, 1908, **25**, 377.

[2] Steubing, *Ann. der Phys.*, 1908, **26**, 329.

R. Gans[3] has considered the problem of the scattering of light by very small ellipsoidal particles. In a theoretical paper he has extended the calculations of the absorption and the scattering of light in gold sols by generalising the shape of the particles into an ellipsoid of rotation, which may be either prolate or oblate, the size of the particles being assumed to be small compared with the wave-length of light. He has shown that as soon as the spherical shape is departed from appreciably, the curve of absorption moves towards the less refrangible end of the spectrum, whether the sphere is flattened or elongated. He has derived expressions for ρ_u and ρ_v for ellipsoidal particles possessing rotation symmetry, where ρ_u and ρ_v are the so-called depolarisations or the measures of the imperfection of polarisation of the light scattered in the transverse horizontal direction when the incident beam is unpolarised and polarised with vibrations vertical respectively. The quantities ρ_u and ρ_u are connected by the following relation :

$$\rho_u = \frac{2\,\rho_v}{1+\rho_v} \tag{1}$$

From the considerations of Gans, it follows that the light scattered by very small ellipsoidal particles in the transverse horizontal direction when the incident beam is polarised with vibrations horizontal should be unpolarised, *i.e.*, ρ_h is equal to unity. If the restriction regarding the size of the particles is not satisfied, the relation (1) is no longer valid. The author[4] has already shown in an earlier paper both experimentally and theoretically that there is a more general relation connecting ρ_u, ρ_v and ρ_h which is valid also for particles of larger size, namely :—

$$\rho_u = \frac{1 + 1/\rho_h}{1 + 1/\rho_v} \tag{2}$$

Relation (2) reduces to (1) when ρ_h = unity. The values of the three quantities both absolutely and relative to each other are a measure of the size, shape and structure of colloidal particles. D. S. Subbaramaiya[5] has measured the values of ρ_u, ρ_v and ρ_h for a series of six gold sols using incident white light. He has shown that in the case of Zsigmondy's blue sol, relation (2) but not relation (1) is satisfied, ρ_h being as small as 54%. No definite conclusions can, however, be derived as regards the size and shape of the gold particles from a measurement of the depolarisation values, ρ_u, ρ_v and ρ_h with incident white light alone ; for, the optical constants of gold, indeed also of any metal, depend very much on the wave-length of

[3] R. Gans, *Ann. der Phys.*, 1912, **37**, 883.

[4] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 782.

[5] D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 358.

light, and measurements of depolarisation made with white light are therefore inadequate.

In some unpublished investigations, Mr. D. S. Subbaramaiya used sunlight filtered through coloured glasses and found in gold sols a marked dependence of the degree of depolarisation on wave-length. Lange[6] had earlier made a careful study of the depolarisation and light absorption of colloidal gold solutions over the wave-length range from 4250 A.U. to 7000 A.U. He has measured the depolarisation factor ρ_u but not the other two quantities ρ_v and ρ_h. From a measurement of ρ_u alone, no definite conclusions can be arrived at regarding the size and shape of the particles, since ρ_v and not ρ_u is the indicator of the optical anisotropy of the particles. Considering the inadequateness of the experimental data even in the classical case of gold sols, it was thought desirable to determine the dispersion of the depolarisation factors ρ_u, ρ_v and ρ_h of the light scattered by the gold sols corresponding to the three states of polarisation of the incident light, over a wide range of wave-length, say from 2500 A.U. to 7000 A.U. In order to make the investigation complete, the absorption of light by the same gold sols has also been measured.

The study of the dispersion of depolarisation of light scattering in colloids is very important since it is connected not only with the size and shape of the particles, but also with other well-known phenomena, such as magnetic, electric and flow birefringence and their dispersion with wave-length exhibited by the colloidal solutions.

2. *Preparation of the Gold Sols.*

The gold sols were prepared by Mr. D. S. Subbaramaiya to whom the author's thanks are due. The details of the preparation of the six gold sols are described by him in his paper.[7] The sols I and II were nuclear sols containing particles of extremely small size. The sols III, IV and V were prepared by the addition of nuclear sol to chlorauric acid solution and reduction by hydrogen peroxide. These sols were red in colour. The sol VI was a blue sol prepared according to the method suggested by Zsigmondy. The sols were preserved in resistance glass bottles thoroughly cleaned and well steamed. The sols were taken as optically infinitely dilute, for on further dilution the colour of the sols remained unchanged.

3. *Depolarisation Measurements.*

Measurements of depolarisation were made separately for the ultra-violet and for the visible regions. For the ultra-violet region a point-light

[6] B. Lange, *Zeits. f. Phys. Chemie*, 1928, 132, 27.

[7] D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, (A), 1935, 2, 358.

quartz mercury arc lamp was used as the source of light, the scattered light being analysed through a Hilger quartz spectrograph. The experimental set up is shown in the accompanying Fig. 1.

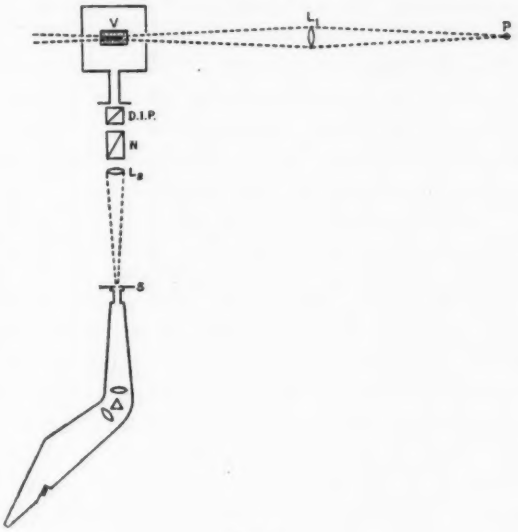

FIG. 1.

P =Point-light mercury arc.
L_1 and L_2=Long focus quartz lens.
D.I.P. =Double-image prism.
N =Nicol which transmits the ultra-violet region also.
V =Quartz cell containing the sol under investigation.

The details of the experiments have already been described in one of the earlier papers of the author.[8] From a series of photographs taken the readings of the nicol corresponding to the equality of intensity of the two components of the scattered light for the two wave-lengths, 2967 and 3650 A.U. were read off and the depolarisation values were calculated therefrom.

For the visible region, the method adopted was slightly different. The light from a 500 c.p. pointolite lamp was condensed on a square aperture (2 mm. square). The illuminated aperture was used as the source of light

[8] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1936, **3**, 566.

instead of the point-light mercury arc. The rest of the experimental arrangement was similar to that shown in Fig. 1. A Fuess glass spectrograph of large dispersion was used instead of the quartz spectrograph. The slit of the spectrograph was kept rather wide. The orientation of the nicol was adjusted so that the two components of the scattered light as seen through the spectrograph were almost of equal intensity for a particular wave-length. One photograph was taken for this position of the nicol. In this manner, for each sol two photographs, one corresponding to incident light unpolarised and the other corresponding to incident light polarised with vibrations vertical, were taken on the same plate along with an iron arc spectrum. Ilford hypersensitive panchromatic plates were used throughout. A series of graded intensity marks was obtained on another plate by photographing the spectrum of a tungsten straight filament lamp with different slit widths, but keeping the time of exposure constant. With the aid of a Moll microphotometer the density log intensity curves were plotted for the following wave-lengths, 4000, 4500, 5000, 5500, 6000, 6500 and 7000 A.U. All the negatives were microphotographed. The ratio of the intensities of the horizontal and the vertical components of the scattered light for each individual wave-length was calculated from the density log intensity curve. From a knowledge of this ratio and the corresponding orientation of the nicol the depolarisation for any particular wave-length could be calculated. Thus the values of ρ_u and ρ_v were calculated.

A correction arising from the finite angle of convergence of the incident beam had to be applied to the observed values of the depolarisation. The angle of convergence ω was $1/7$ of a radian. Consequently, the convergence correction for ρ_u is $\omega^2/8 = 0{\cdot}25\%$. The correction for ρ_v is half of that for ρ_u. The corrected values of ρ_u and ρ_v are given in Tables I and II. ρ_h was calculated from the observed values of ρ_u and ρ_v using the relation (2). In a few cases owing to a small experimental error in the determination of either ρ_u or ρ_v the calculated value of ρ_h was found to be slightly greater than 100%. In such cases ρ_h was put equal to 100%.

TABLE I. *Dispersion of Depolarisation.*

Wave-length	Gold sol I			Gold sol II			Gold sol III		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	3·8	2·2	100	4	2·1	100	3·4	1·6	86
3650	4	2·2	100	3·8	2	100	3·4	1·6	86
4000	4·6	2·4	100	3	1·59	100	4·6	2·4	100
4500	4·6	2·5	100	3·9	1·76	83	4·75	2·4	98
5000	6·2	3·1	100	4·5	2·2	92	7·2	3·9	100
5500	8	4·4	100	12·3	6·4	100	18	10·6	100
6000	14	8	100	13	6·6	100	29·5	16	100
6500	16	9·2	100	16·3	9	100	16	9	100
7000	..	..	..	10·9	6	100	16	9	100

TABLE II. *Dispersion of Depolarisation.*

Wave-length	Gold sol IV			Gold sol V			Gold sol VI		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	3·1	1·5	91	3	1·3	75	..	..	..
3650	3·1	1·6	100	3	1·4	85	5·5	2·1	60
4000	3·6	1·7	86	2·4	0·9	59	5·0	1·7	50
4500	3·2	1·75	100	2·5	1·5	100	4·6	1·6	52
5000	3·8	2·2	100	6	3·2	100	5·2	1·9	65
5500	14·3	7·85	100	13	7	100	12·7	6	80
6000	16·3	9	100	13·6	7·8	100	17	8·4	84
6500	16·5	9·3	100	14·6	8	100	18·8	10	94
7000	16·8	9·7	100	15·3	8·2	100	22·7	12·7	97

The values of ρ_u were plotted against wave-length. The curves are reproduced in Figs. 2 and 3.

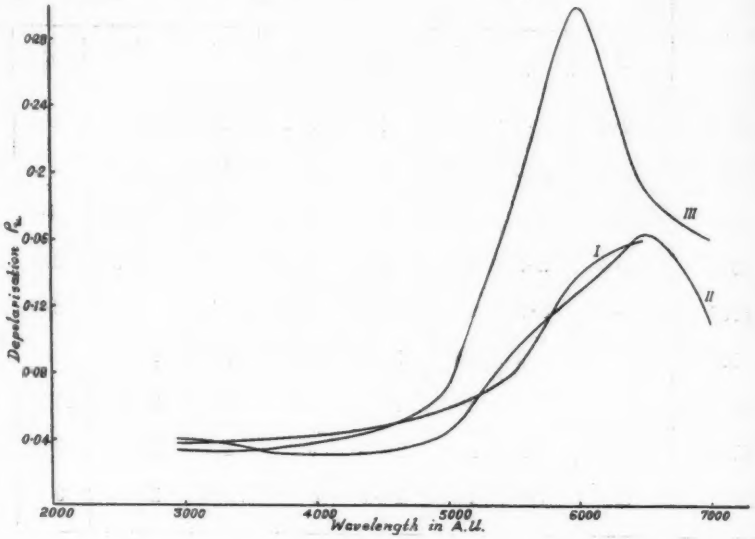

FIG. 2.

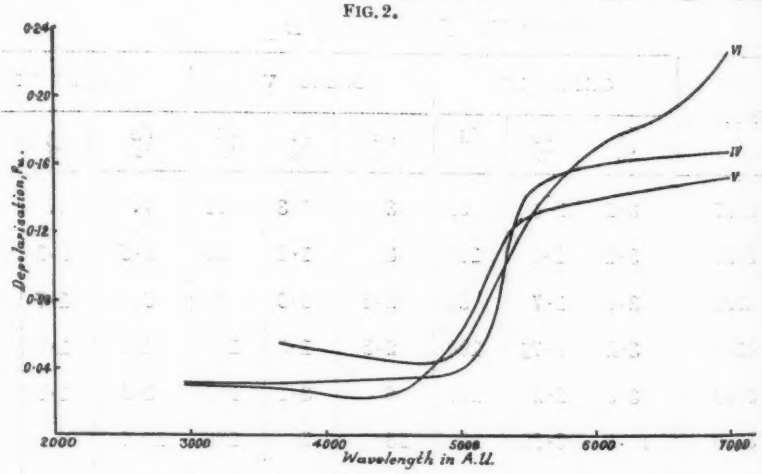

FIG. 3.

4. Absorption Measurements.

The absorption measurements were made with a Spekker ultra-violet photometer and a quartz spectrograph. The source of ultra-violet radiation

was the condenser spark between two tungsten steel electrodes. To correct for the reflections of the end plates of the tube containing the sol under examination, a similar tube was used in the second light path of the photometer, this tube being filled with pure double-distilled water. The extinction coefficient $\left(\log \frac{I'}{I}\right)\Big/D$ was determined for a series of wave-lengths from 2500 A.U. to 7000 A.U. D is the thickness of the cell in centimetres. The values of the extinction coefficients are given in Table III.

TABLE III.

Extinction Coefficient of Gold Sols.

λ	I	II	III	IV	V	VI
2250	0·75	0·57	0·9	0·575	0·575	>3
2500	0·7	0·55	0·9	0·575	0·575	>3
2750	0·65	0·5	0·8	0·53	0·49	>3
3000	0 6	0·42	0·65	0·5	0·425	>3
3250	0·525	0·37	0·55	0·45	0·35	1·3
3500	0·4	0·35	0·525	0·4	0·3	0·75
3750	0·4	0·32	0·47	0·37	0·29	0·6
4000	0·375	0·30	0·45	0·35	0·275	0·475
4250	0·35	0·29	0·425	0·35	0·275	0·45
4500	0·3	0·3	0·4	0·325	0·26	0·425
5000	0·35	0·32	0·575	0·46	0·4	0·45
5250	0·4	0·42	0·84	0·76	0·55	0·52
5500	0·35	0·38	0·56	0·575	0·55	0·525
6000	0·25	0·2	0·225	0·35	0·2	0·5
6500	0·15	0·125	0·125	0·15	0·125	0·475
7000	0·1	0·1	0·09	0·09	0·062	0·45

The curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ.

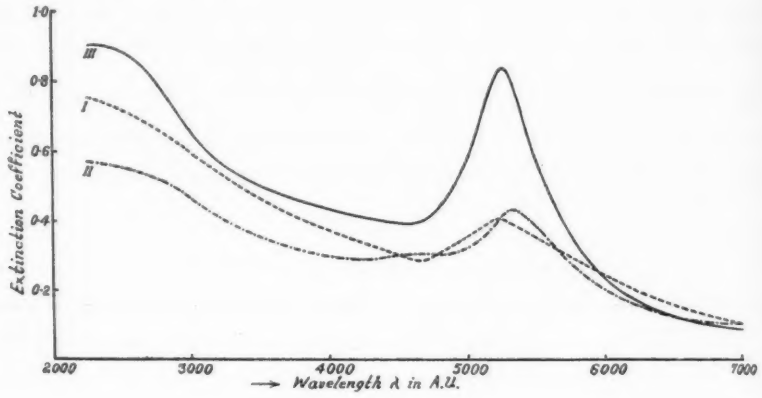

FIG. 4

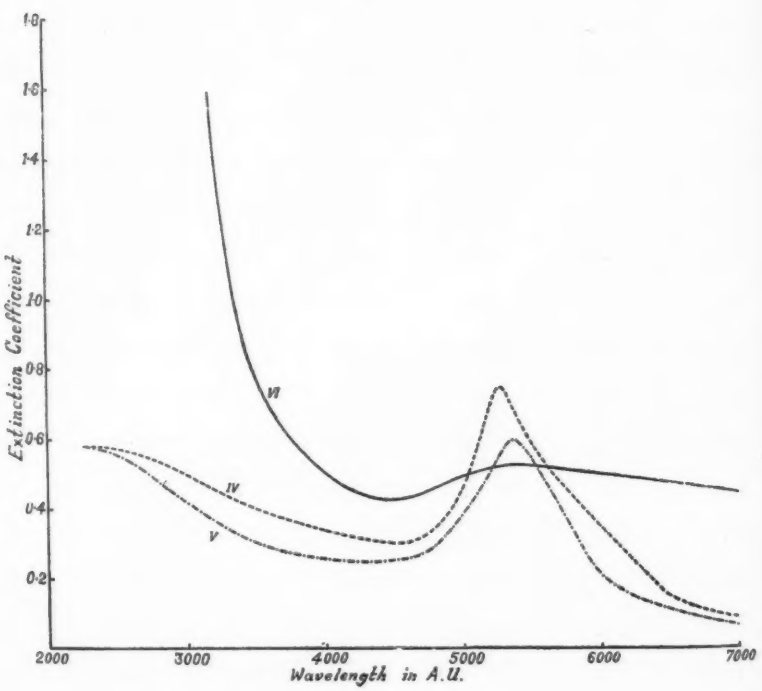

FIG. 5.

5. *Results.*

In all the sols studied it is found that ρ_u is markedly a function of wave-length. In the case of sols II and III after attaining a maximum in the region of the characteristic absorption, ρ_u diminishes with further increase of wave-length. In the case of the last two sols the value of ρ_u goes on diminishing at first and then it increases. ρ_v follows the same course as ρ_u. For the first three sols ρ_h has its limiting value of 100% from λ 2500 to 7000 A.U. For the sols IV and V ρ_h is definitely less than 100% in the ultra-violet region. In the blue sol ρ_h is less than 100% throughout, and increases or decreases with wave-length *pari passu* with ρ_u. In the region of the characteristic absorption there is an increase of the optical anisotropy as is shown by the notable increase of ρ_v. A comparative study of the values of ρ_h for all the sols shows that sols I, II and III contain particles whose size is of the order of molecular dimensions, while, in sol VI the size of the particle is comparable with the wave-length of light. The sols IV and V contain particles of intermediate sizes. The fact that ρ_u has the same low value for almost all the sols at about 3000 A.U. indicates that the anisotropy of shape of the particles is small and is independent of the method of preparation of the sol and also of the particle size, provided the latter is small compared with the wave-length of light. This is not surprising, for the sols III to VI are prepared using the nuclear sol I, and consequently it is natural to expect the general shape of the particles in the nuclear sol to be retained in the other sols also. The small increase in the value of ρ_u below 4000 A.U. evinced by the sols V and VI is a size effect.

As has been observed previously, the curves of absorption show a pronounced maximum in the green region, *i.e.*, at about 5250 A.U., for all the sols except for the blue sol. The actual value of the extinction coefficient goes on increasing from sol I to sol IV, while, it goes on decreasing from sol IV to sol VI. It is found that the maximum of the absorption curve is shifted towards the longer wave-length side as one goes from sol I to sol VI. In all the sols studied the absorption increases again in the ultra-violet region.

6. *Theoretical Discussion.*

According to Gans's theory, for a flattened rotation ellipsoid the maximum of the depolarisation curve should lie in the green region, *i.e.*, at about 5250 A.U., whereas for an elongated ellipsoid or a prolate spheroid the maximum is shifted towards the longer wave-length side. The latter corresponds to the experimentally observed data. Table IV gives the comparative values of the depolarisation ρ_u calculated according to Gans's

formula for very small particles of ellipsoidal shape. The values are taken from Lange's paper.[9] The values of ρ_u for an elongated rotation ellipsoid with axial ratio B/A = 0·7 have been obtained by interpolation.

TABLE IV.

Values of ρ_u (calculated).

	Elongated rotation ellipsoid				Sphere	Flattened rotation ellipsoid			
B/A / λ in A. U.	0·00 %	0·57 %	0·70 %	0·82 %	1·00 %	1·28 %	2·63 %	6·25 %	∞ %
4200	35·8	4·7	2	0·49	0·0	8·84	9·3	20·5	30·6
4500	37·9	4·4	1·9	0·49	0·0	0·86	9·4	20·5	30·5
5000	76·6	32·3	10	1·48	0·0	2·06	19·1	36·1	19·1
5250	40·3	28·2	10·5	3·12	0·0	3·51	26·3	44·2	55·9
5500	47·8	51·8	21	4·6	0·0	2·36	28·1	37·9	56·1
6000	87·4	17·1	6	2·0	0·0	1·79	6·5	37·4	48·1
6500	2·2	10·5	4·5	1·2	0·0	0·98	5·6	32·0	41·6

Comparing the theoretical values of the depolarisation ρ_u witn the experimental values, it is seen that the particles in the gold sol are more like elongated rotation ellipsoids with the axes ratio B/A = 0·7. In the case of the sols IV, V and VI the observed value of ρ_u goes on increasing continuously with wave-length. This may be due to the finite size of the particles. The theory of Gans is only true for particles of extremely small size.

It is not difficult to explain the observed values of the extinction coefficient provided it is assumed that the particles are prolate ellipsoids and that the deviation from spherical shape is small. The following table gives the absorption constant $k \times 10^{-3}$ for different wave-lengths caclulated according to Gans, for very small particles of ellipsoidal shape. k is defined given by the equation $I = I_0\, e^{-kcx}$, where x is the thickness of the layer in millimetres. For a sol containing one millimetre cube of gold by volume per litre of the sol, c is equal to 10^{-6}. The values are taken from Gans's paper.[10]

[9] B. Lange, *Loc. cit.*

[10] R. Gans, *Loc. cit.*

The values of k given in the table below for an elongated rotation ellipsoid with the axes ratio B/A = 0·7 are obtained by interpolation. A comparative study of the Tables III and V shows at once that although the experimentally determined absorption curves are similar to the theoretical curves calculated according to Mie's theory for spherical particles, there is better agreement between the observed curves and the curves calculated according to the theory of Gans for elongated rotation ellipsoidal particles having an axial ratio equal to 0·75. From the above discussion it can be said with certainty that the particles in the gold sols studied are not spherical in shape but behave as elongated ellipsoids with the axial ratio B/A of the order of magnitude stated.

TABLE V.

Absorption Coefficient.

	Elongated rotation ellipsoid				Sphere	Flattened rotation ellipsoid			
B/A / λ in A. U.	0·00	0·57	0·70	0·77	1·00	1·61	2·63	45	∞
4200	36·7	41·8	41·3	41·0	40·6	42·4	46·4	48·3	44·9
4500	34·5	38·8	38·1	37·8	37·4	39·1	43·6	45·7	43·3
5000	30·9	57·3	58·7	59·4	59·2	62·2	64·0	60·0	29·5
5250	24·5	68·6	71·0	72·3	69·1	82·7	87·4	75·8	22·2
5500	18·7	83·0	71·5	67·3	55·2	89·0	131·5	102·9	16·6
6000	8·7	68·7	33·5	21·6	16·4	29·5	126·9	262·5	12·0
6500	8·5	18·0	9·5	8·3	6·92	10·5	31·0	77·2	14·2

7. *Other Experimental Evidence.*

The double refraction in gold sols produced by mechanical flow has been investigated by Bjornstahl[11] and S. Berkman, J. Boehm and H. Zocher.[12] According to them all the gold sols except the sol prepared by Zsigmondy's formaline method show a negative streaming double refraction indicating thereby that the particles are not spherical in shape, but are elongated. The influence of the wave-length is very pronounced; the effect can be scarcely observed in the violet region whereas it is great in the red region.

[11] Y. Bjornstahl, *Inaugural Dissertation*, Upsala, 1924.

[12] S. Berkman, J. Boehm and H. Zocher, *Zeits. f. Phys. Chemie*, 1926, **124**, 83.

This type of dispersion of flow birefringence is generally anomalous. But in the light of the present investigation it finds an easy explanation. Depolarisation measurements indicate that the optical anisotropy is much greater in the red region than in the violet region. Since the intensity of scattering is also great in this region of the spectrum, the refraction should necessarily increase with wave-length. In consequence of this the double refraction produced by mechanical flow should also exhibit a similar dispersion. This is actually the case. From a knowledge of the dispersion of refractive index of the colloidal solution and the anisotropy of shape calculated from the depolarisation measurements, it should be possible to calculate the magnitude of the streaming double refraction in these colloidal solutions and also its dispersion with wave-length.

Gold sols should not exhibit any appreciable magnetic double refraction since gold is diamagnetically isotropic, and since X-ray analysis discloses that the particles in the colloidal state exhibit a crystal structure similar to that of gold in mass. This is in accordance with recent observations with gold sols which fail to exhibit magnetic double refraction made by Mr. P. Nilakantan[13] in this laboratory. It is difficult to understand how Bjornstahl[14] observed a considerable magnetic double refraction in gold sols prepared by the nuclear method using hydrogen peroxide as the reducing agent. Assuming for the present that the observed magnetic anisotropy in his experiments was due to the presence of a small trace of some impurity (say iron), the large dispersion of magnetic double refraction observed by him finds an easy explanation on the same lines as indicated in the previous paragraph.

8. *Summary.*

The earlier investigations (theoretical as well as experimental) on the light scattering and absorption of gold sols have been briefly reviewed. It is pointed out that in order to determine the size and shape of colloidal particles, it is important to make comparative studies of the dispersion of depolarisation of the transversely scattered light with the incident light in three different states of polarisation, namely, unpolarised, vertically polarised and horizontally polarised. Measurements of the depolarisation factors ρ_u and ρ_v and the extinction coefficient of a series of six gold sols are made for different wave-lengths from 2500 A.U. to 7000 A.U. The value of ρ_h is calculated from the observed values of ρ_u and ρ_v using the reciprocity relation. In the region of the characteristic absorption the

[13] P. Nilakantan, *Unpublished work.*

[14] Bjornstahl, *Loc. cit.*

depolarisation factors show an enormous increase. The optical anisotropy of the gold particles in the colloidal state is rather low in the shorter wave-length region, whereas it assumes rather high values in the green region where the absorption is maximum. The observed values of the extinction coefficient and the depolarisation factor ρ_u are compared with the values calculated according to Gans's theory. From both of these considerations, it is inferred that the particles in the gold sols behave optically like elongated ellipsoids with the axial ratio equal to about 0·75. The values of ρ_h indicate that the size of the particles in the nuclear sols is small compared with the wave-length of light, while the blue sol contains particles of size comparable with the wave-length of light. The negative streaming double refraction and its dispersion with wave-length observed by the earlier investigators are explained on the basis of the elongated ellipsoidal shape of the particles and the dispersion of their optical anisotropy.

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